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THE CORROSION OF IRON AND STEEL

BY

J. NEWTON FRIEND, Ph.D. (Würz.), D.Sc. (B'ham)

FELLOW OF THE CHEMICAL SOCIETY, MEMBER OF THE IRON AND
STEEL INSTITUTE

AUTHOR OF "THE THEORY OF VALENCY," "AN INTRODUCTION TO THE CHEMISTRY
OF PAINTS," "ANALYTICAL TABLES"

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TO MY

FATHER AND MOTHER

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PREFACE

DURING the last few years the civilized world has begun to realize the importance of understanding the numerous factors connected with the corrosion of iron. Iron is being manufactured in enormous quantities at the present day, and is used for almost every conceivable purpose, so that it is essential for us to gain some knowledge of its powers of resistance to the destructive action of time. Numerous researches have therefore been undertaken with a view to solving one or other of the problems in question, and it seemed desirable to collect all the reliable material together and present it to the scientific public generally, in order that the manufacturers and consumers alike might easily learn how much is actually known of the subject, and in what direction further research is desirable. This has been particularly needful, inasmuch as those who have published works have frequently been manifestly ignorant of the work of previous investigators along similar lines, and it is remarkable what a number of times certain facts have been discovered and rediscovered. Take for example the fact, apparently first proved experimentally by Adie in 1845, that saturated solutions of common salt do not corrode iron in the presence of air with anything like the rapidity that tap water does. No fewer than three different investigators have rediscovered this fact independently at later dates and commented upon their remarkable observation. Numerous other examples might be quoted, but the above is sufficient. Nor is the reason far to seek; the literature on corrosion is so vast and so widely scattered that it has hitherto been exceedingly difficult to become thoroughly acquainted with it. The present work is the outcome of an attempt to review all the reliable work done on the subject.

The task has not been easy, for it has necessitated the careful study of many hundreds of memoirs, not only in order that the numerous misstatements with regard to priority might be corrected, but that explanations might be found for the lack of agreement between the results of different investigators—a sign that some important factor in experimentation has been overlooked.

Many of the original memoirs are now out of print and not easily accessible; and it is at once my privilege and pleasure to acknowledge the kind assistance rendered to me by authors, librarians, and interested persons who have afforded me special opportunities for studying memoirs and works to which I could not otherwise have gained access. My heartiest thanks in this connexion are due to Professors Thomas Turner of Birmingham University, E. Heyn of Berlin, William H. Walker of Massachusetts, and H. M. Howe of New York; to Drs. Gerald T. Moody, A. S. Cushman, and J. E. Stead; and to Messrs. Fredk. Jno. Rowan, A.M.I.C.E., Alexander Frazer, Henry L. Heathcote, A. Campion, Bertram Lambert of Oxford, and James McMillan.

In addition to these, I gratefully acknowledge the kindness of the Librarian and his Staff at the Darlington Public Library, and of Mr. G. C. Lloyd, Secretary of the

Iron and Steel Institute, all of whom in one way and another have afforded me special opportunities of arriving at the solution of numerous literary problems in connexion with this work.

My thanks are likewise due to the Council of the Chemical Society for permitting me to reproduce the diagrams in Figs. 5, 9, 11, and 12, and to the Authors of the papers from which these diagrams were taken. I am likewise indebted to the American Rolling Mill Company, Ohio, for certain particulars concerning their iron, to which reference is made in several parts of the text, and for sending me samples of their metal for the sake of comparison.

Finally, my best thanks are due to my Wife, who has patiently checked the numerous references in the text, and afforded me untiring assistance in arranging the Indexes.

Nowadays it is often a difficult task for the beginner anxious to do research work to find a suitable subject. The careful Reader can scarcely peruse these pages, however, without realizing what an immense amount of work still requires to be done in this particular field. It has been my endeavour, therefore, to make the lists of references bearing on each point under discussion as complete and up-to-date as possible, in order that the Reader wishing to pursue the subject further may be enabled to do so with the minimum loss of time. If he be thereby stimulated to pursue some research on his own account and thus to assist in causing the boundary between the known and the unknown to recede, one of the objects of this work will be achieved.

Every endeavour has been made to render the information accurate, and to give each Author his due.

Should any investigators find that their work has been overlooked I shall be very glad if they will communicate with me at once, so that in any future editions the matter may be put right.

It will be observed that the question of the protection of iron and steel has only been dealt with in so far as it concerns the problems of corrosion. I have been collecting material for some time on this important question, and should the sale of the present work be sufficiently encouraging, it is my intention to devote a companion volume to its consideration.

J. NEWTON FRIEND.

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I.

IRON, ITS HISTORY AND ECONOMIC VALUE.

Few historical problems are of more absorbing interest than those connected with the early history and use of iron.[1] That this metal has been used for thousands of years by man is now a well-established fact. Those monumental works of Egypt, known as the pyramids, were erected to the honour of potent monarchs some 3000 B.C. The Great Pyramid at Gizeh, for example, is built of granite blocks hailing from the upper Nile and is lined with Arabian nummulitic limestone. The marvellous skill with which these granite blocks are worked apparently points to the use of iron tools, for no other material would be sufficiently hard and serviceable. The correctness of this deduction received confirmation in 1837 by the discovery, during blasting operations within the Great Pyramid, of a wrought iron tool, which is thus approximately 5000 years old.[2] Analysis showed it to contain a small quantity of nickel, and of combined carbon, which latter fact shows that it could scarcely be of meteoric origin. Iron, therefore, was evidently worked even at that early date, although, perhaps, to but a very limited extent, by the Egyptians. It does not of necessity follow, however, that, because comparatively few iron tools have been discovered which undoubtedly date back to such remote periods in the history of civilization, therefore the iron industry was not in a flourishing condition. As we all know to our cost, the metal is so liable to corrode that a tool, left in any exposed place, would be rapidly converted into rust, and this, in process of time, might entirely disappear in consequence of the solvent action of organic acids present in humus and decaying vegetable matter, leaving no indication whatever of its having been there. Nevertheless, much of the iron used in Egypt is believed to have found its way there from Ethiopia, which latter country was probably the first to practise iron smelting. R. D. George[1] adduces evidence to show that iron probably never found wide favour in ancient Egypt, although it was used side by side with bronze tools.

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[1] An excellent account of the early history of iron has been given by Bennett H. Brough, "J. Iron Steel Inst." 1906, I, 233-53."

[2] See J. V. Day, "Proc. Phil. Soc. Glasgow," 12 April, 1871. The tool is 9 inches long and less than 3 inches broad. Its use is doubtful.

The Israelites knew how to work iron, as is evidenced by several interesting allusions in the Holy Scriptures,[2] where furnaces and instruments of iron are mentioned, as well as artificers skilled in the manipulation of the same. The Amorite giant, Og, king of Bashan, defeated by the Israelites at Edrei some 1200 B.C. possessed an iron bedstead, "nine cubits was the length thereof, and four cubits the breadth of it, after the cubit of a man".[3] In Josh. x. 31-2 we are told that "Joshua passed from Libnah, and all Israel with him, unto Lachish, and encamped against it and . . . took it on the second day". The city was deserted by the Israelites about 400 B.C. Nevertheless Petrie found amongst its ruins tools of iron and bronze, clearly proving that their use was known to the Israelites.

The ancient Chinese appear to have been familiar with metallic iron as far back as 2357 B.C., as recent researches into the history of that curious people show.

Our forefathers, the Aryans, in India used iron of very high quality. The remarkable pillar at Delhi, which measures 50 feet in height and 16 inches in diameter, is composed of a series of blooms each weighing approximately 50 lb. and welded together. It is stated to date back to the year 912 B.C., and is remarkably free from rust, its surface being merely tarnished.[1]

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[1] R. D. George, "Popular Science Monthly," **67**, 687.

[2] See Gen. IV. 22; Deut. IV. 20; Num. XXXV. 16, etc.

[3] Deut. III. II. Assuming the cubit to be 20·6 inches, the dimensions of the bed were approximately 15·5 × 7 feet.

From Western Asia and Egypt the path of civilization extended westward to Greece. Montelius,[2] believes that the first use of iron in this last-named country dates back as far as 1400 B.C. Homer, 880 B.C., refers to "iron wrought with much toil," and the Spartans are well known to have worn rings of iron, and to have bartered goods with bars of the same metal some 300 years before Christ. Further, Schliemann discovered fragments of iron amid the ruins of ancient Mycenæ, a city destroyed 561 B.C.

With the rise of the Roman nation the knowledge of iron was pushed yet farther westward, and all the important European mines fell into their hands. Julius Cæsar, however, states that he found the early British using iron bars for coin when he visited our island, and Reginald A. Smith[3] has recently been able to throw still more light upon this early custom, by describing a remarkable series of early British iron bars, weighing 4770 grains, 2 × 4770 grains, and 4 × 4770 grains, respectively, which are undoubtedly some of the bars alluded to by Cæsar. A few of these lie in the British Museum. C. Wilkins[4] locates S. Wales as the early home of the iron trade, and gives reasons for believing that the British bars above referred to were made from iron ore mined in the Taff Vale. In A.D. 120, Emperor Hadrian founded an arms factory at Bath where iron from the Forest of Dean was worked. The Romans evidently appreciated the value of iron and established forges at various camps and cities throughout their empire,[5] using the metal freely in agriculture, war, and the arts of peace generally.

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[1] See p. 231, where this freedom from corrosion is discussed.

[2] Montelius, "J. Iron Steel Inst."1900, II, 514.

[3] R. A. Smith, "Proc. Soc. Antiq." XX, 179. See also "A Guide to the Antiquities of the Early Iron Age in the British Museum," by R. A. Smith. London, 1905.

[4] C. Wilkins, "The History of the Iron, Steel, Tinplate, and other trades of Wales". Merthyr Tydfil, 1903.

[5] See Scrivenor, "History of the Iron Trade". Longmans & Co. 1854, p. 29.

In our own island the iron trade has had a very chequered existence. During the Roman occupation steel and iron were extensively manufactured, but the unsettled rule of the Saxons led to its neglect until the advent of the eleventh century, when it began to revive. At the Norman Conquest the iron trade was in a flourishing condition, but the lawless government of the turbulent barons again caused a depression, and iron became a rare and costly material. During the Middle Ages iron was manufactured in several parts of the country, and in 1350 or thereabouts cast iron was produced in Sussex. In the reign of Elizabeth trade declined owing to the scarcity of charcoal, which was the only fuel used; but when the value of coal was realized, and the various Acts of Parliament prohibiting its use were revoked, iron manufacture again flourished, so that, at the beginning of the nineteenth century blast furnaces, 40 feet in height and of 2000 cubic feet capacity, were in regular use, and the average annual amount of pig iron produced was nearly half a million tons. Since that time the trade has progressed by leaps and bounds until its present state has been reached.

The average individual, however, does not appear to be aware of the great debt which we owe to iron. It is not too much to say that the world could never have reached such an exalted state of civilization and luxury, had it not been supplied with an abundant supply of iron. Without this metal our knowledge of electricity must have been wofully limited, and an extended application of the same a practical impossibility. Iron is an important factor in the construction of our ships and our railroads. Steel bridges and iron frames for our more important buildings are the order of the day. For domestic purposes iron is now likewise indispensable. By means of iron pipes both gas and water are conducted to our houses; our kitchens are equipped with iron stoves and ranges; whilst the very keys, by which we gain entrance to our rooms, are made of the same material. What wonder, then, that scientists have spent long years, taxing their ingenuity to the utmost, in order to elucidate the numerous problems connected with the origin, working, and practical use of this all-important metal.

The enormous quantities of iron employed by the civilized nations of to-day are far too large to be adequately comprehended, and the rate of consumption of iron ore has increased within the last few years at an appalling rate, as the following figures will show:—

Year.	Pig Iron produced. (Millions of tons).
1800	0·5
1850	4
1900	40
1904	46
1909	60

These data are shown graphically in Fig. 1.

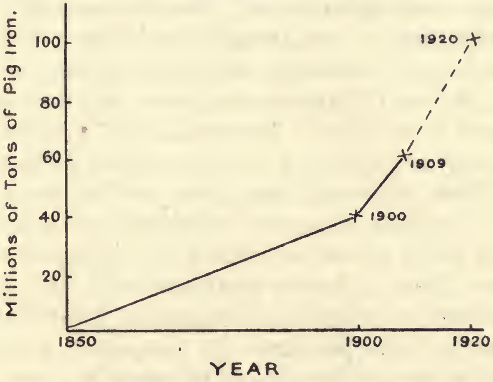

FIGURE I.—CURVE ILLUSTRATING THE ANNUAL PRODUCTIONS OF PIG IRON SINCE 1800.

The thoughtful reader cannot fail to ask himself the question—Where will this consumption end? If we continue the curve, as indicated by the broken line in the figure, we see that in 1920 the annual production of pig iron will reach the unprecedented amount of 100 million tons, corresponding to a consumption of practically twice that weight of ore—provided, of course, the demand continues to increase at the same steady rate that has characterized the past five years. It must be obvious to every one that, unless our stores of iron are absolutely inexhaustible, we must very soon be face to face with an iron famine should we continue to draw upon those stores with such a prodigal hand. Although it is impossible to say with certainty how much accessible iron ore exists in the earth's crust,[1] we have every reason to believe that its amount is not inexhaustible, and it is a duty which we owe to our descendants that we exert due economy and make our stores last as long as we conveniently can.

But even supposing for a moment that our supplies of ore are indeed inexhaustible, is such also true of coal and fuel generally? We often fail to realize that about 4 tons of coal or their equivalent are used in extracting and preparing a single ton of steel from the ore. Now the world could exist, if not indeed flourish, even though far less iron were used than is now customary; but could civilization continue if deprived of coal? The man in the street at once falls back upon the magic name of electricity. But we must not overlook the fact that almost all the electricity in this country is produced at the expense of coal, and unless some new source of energy is found, or fresh methods are invented for utilizing those forces of nature of which we have not yet full control, the supply of electricity will always be limited by the plentifulness of fuel. The coal question, therefore, rivals in importance, if, indeed, it does not even excel, the iron problem. At the present rates of consumption the coal in Britain and Germany may last for from 500 to 1000 years, and the United States have apparently sufficient for 6000 years. But if the consumption persists in increasing at its present rate, all the coal seams that can be worked under existing conditions will be used up in about 150 years.

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[1] See S. Philipp, "Stahl und Eisen," 1909, **29**, 1952; R. A. Hadfield, "J. Iron Steel Inst.," 1905, I, 59. See also discussions on coal and iron at the Eleventh International Geological Congress, at Stockholm, August, 1910, reported in "Nature," 6 October, 1910; also the Reports of the U.S. Geological Survey, abstracted in "Nature," 20 October, 1910.

Now one of the most important ways by which we can conserve our stores, both of iron and of fuel, lies undoubtedly in the prolonging of the life of those iron articles already in use, by either protecting them against corrosion, or rendering the metal itself immune to the attacks of natural forces.

When such metals as lead and copper are exposed to the destructive action of air and moisture, they become coated with a thin film of oxide or insoluble compound, which serves to protect the metal underneath. In this way their life is indefinitely prolonged.

Unfortunately, in the case of iron this is not true. Iron readily rusts in a moist atmosphere, its surface yielding a highly porous, and hygroscopic mass of oxide, which not only fails to protect the underlying metal from attack, but actually stimulates further corrosion, just as a piece of rotten wood causes the decay of sound material in contact with it. The result is that iron kept in exposed places rapidly deteriorates, and has to be constantly replaced.

Any man, therefore, who can find means to arrest this corrosion, and thereby prolong the life of iron, is doing the world an immense service, tantamount to increasing the available supply, not only of the ore, but also of the fuel necessary to reduce it. In order that we may be able to do this, it is essential that we first of all gain an insight into the mechanism of corrosion itself, and it is with the object of assisting my readers to do this that the present work has been written.

II.

THE ACTION OF AIR AND WATER UPON IRON.

It is a matter of common knowledge that when any ordinary grade of commercial iron is exposed to the atmosphere, even for a comparatively short period of time, it rapidly becomes covered with a reddish-brown, porous oxide, to which the name of rust has been given. This is such a well-recognized peculiarity that iron structures situate in exposed places are universally painted or coated with cement, zinc, tin, or other protective material, in order that their life may be prolonged. Such devices, however, are almost as ancient as the hills themselves, having been practised for many centuries. Amongst the ruins of ancient Nimroud, once an opulent Assyrian city, Layard[1] found a number of ornamental objects produced by casting bronze around a core of iron. The early metallurgist, therefore, was aware that iron is stronger and less fusible than bronze, the latter being used to take the required impression and to resist the corrosive action of the atmosphere, whilst the former imparted to the whole article its own strength and firmness. Amongst the remains of the Swiss Lake Dwellings iron similarly protected has not infrequently been found.[2]

But although iron work in certain situations is frequently corroded with such rapidity as to be rendered valueless in the course of a few months, yet in other places it may only suffer slight deterioration during the same period of time—and this in cases where there can be no doubt as to the exact similarity of the metal employed. Clearly, therefore, a thorough understanding of the nature and conditions of atmospheric attack upon iron is a matter of prime importance.

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[1] See the "Guide to the British Museum," 1890, p. 130.

[2] Bennett H. Brough, "J. Iron Steel Inst." 1906, I, 233.

(*a*) ACTION OF DRY AIR UPON IRON.

For many years it has been a matter of common knowledge that a piece of polished and bright iron may be kept for an indefinite time exposed to the dry air without suffering the slightest diminution in metallic splendour, provided, of course, the temperature is not raised abnormally. A very remarkable example of this permanence is given by Zumstein[1] who fixed a polished iron cross on the summit of Monte Rosa, during the month of August, 1820. On visiting the place again in August, 1821, the cross was found to be entirely free from rust, a slight bronze-coloured tarnish alone being observable.[2] The temperature of the air was about – 6° C. so that the amount of water vapour was reduced to a minimum.

Even at 100° C. the action of air upon iron is indefinitely slow. Friend[3] kept a piece of bright iron foil at 100° C. for five hours and could observe no difference in its appearance at the end of this time. The temperature was then raised to 150° C. for a further period of five hours; but even after this treatment it was impossible to decide by mere observation whether or not the surface of the metal was tarnished, for the action was so slight. If the temperature is still further raised the iron gradually unites with the oxygen, the actual extent of oxidation depending both upon the temperature and the length of exposure. As merely superficial oxidation obtains, the skin formed tends to protect the metal beneath from further attack, so that a quantitative measurement of the rate of reaction is rendered very difficult. The layers of oxide produced, however, impart to the iron a characteristic hue, varying from a pale straw to a deep blue, according to their thickness. As this latter is rapidly affected by change of temperature, and only relatively slowly by the length of exposure, the colour of the iron is a fairly accurate indication of its temperature. This fact is largely made use of by workmen in tempering steel, and the following table gives the usually accepted data:—[1]

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[1] Zumstein, "British Association Reports," 1838, p. 255.

[2] No analyses of the metal are given, and the assumption is that the cross was made of ordinary commercial iron of average composition. A similar bronze-like appearance is likewise exhibited by the remarkable prehistoric iron column of Kutab Minar, Delhi, in India, but the climatic differences are so great that a similar explanation will not hold. This latter problem is discussed on p. 231.

[3] Friend, "J. Iron Steel Inst." 1909, II, 172.

Oxide Tint.	Temperature °C.	Temperature °F.
Pale yellow	220	428
Straw	230	446
Golden yellow	243	469
Brown	255	491
Brown and purple	265	509
Purple	277	531
Bright blue	288	550
Full blue	293	559
Dark blue	316	600

That these colours are indeed due to layers of oxide was first demonstrated by Roberts[2] who showed that, if the steels are heated in vacuo, these colours are not produced.

Although the empirical control of tempering by observation of the colour is being superseded by the use of baths of known temperature, the old method has still many advocates, and can be made to yield surprisingly accurate results at the hands of skilful workmen. Nevertheless, despite the arguments of Barus and Strouhal,[3] both general experience and the results of direct experiment show that quite a large number of factors exert their influence upon the temperature at which the above hues are obtained, and that it is only when the conditions are kept very uniform that accurate results may be expected. Thus, L. Loewenherz [1] draws attention to the fact that the degree to which a steel must be heated in order to produce any definite colour depends both on the hardness of the sample and upon its chemical composition, any variation in this latter factor exerting a marked influence. The shape of the metal, too, was found to affect the results slightly.

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[1] H. M. Howe, "The Metallurgy of Steel," 2nd ed. 1891, I, p. 23. New York.

[2] Roberts, "Trans. Inst. Mech. Eng." 1881, p. 710. See also G. Stein, "J. Iron Steel Inst." 1889, II, 460.

[3] C. Barus and V. Strouhal, "Bull. U.S. Geol. Survey," 1886, **27**, 51; C. Barus, "Nature," 1889, **41**, 369.

Mention has already been made of the fact that the length of exposure also determines to some extent the hue produced at any given temperature. This subject has been carefully investigated by Turner, [2] and more recently by Guillet and Portevin.[3] The first-named investigator shows very clearly that any colour may be produced by sufficient heating at a lower temperature than that usually given as corresponding to that hue. For example, a pale straw colour can be obtained at 170° C. by prolonged exposure, whereas 220° C. is the temperature usually accepted as corresponding to it. The time required to pass from hue to hue up the series increases as we ascend the scale. Thus, for example, a few minutes only suffice to pass from pale yellow to straw (220 to 230° C.), but as many hours may be required to change the purple colour into blue (277 to 288° C.) although the temperature difference is but 10° C. in either case. Further, a purple hue can be obtained in a few minutes at 250° C., and in an hour at 220° C., but at 170° C. no fewer than twelve hours are required.

This is, of course, to be expected, for an increase in thickness of the oxide layers must take place almost entirely by diffusion—a process which becomes increasingly slower as the temperature falls or as the depth below the surface advances.

Turner further shows that the colour obtained depends to some extent upon local conditions, such as, for example, roughness, dirt, etc. By heating steel in an air-bath, whilst lying on a copper plate to ensure uniformity of temperature, it was found that rough iron gave the same general hue as smooth, but that it was not so brilliant. Some kinds of dirt appeared to retard oxidation and others to assist it.

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[1] L. Loewenherz, "Zeitsch. Instrumentenkunde," 9, 316; "J. Iron Steel Inst." 1889, II, 460.

[2] T. Turner, "Proc. Birm. Phil. Soc." 1889, VI, part ii.

[3] L. Guillet and A. Portevin, "Revue Métallurgie: Mémoires," VI, pp. 102-4; from "J. Iron Steel Inst." 1909, I, 647.

These tempering colours appear in the presence of even such dry air as that obtained by storage over phosphorus pentoxide for several months. Friend[1] sealed a piece of Kahlbaum's pure iron foil in a glass tube together with some phosphorus pentoxide, the two being separated by means of glass wool. After the lapse of four months the end containing the iron was immersed in an oil-bath at 190° C. for thirty minutes. As the change produced was slight, the temperature was raised to 220° C. when, after the expiration of a second half hour, the iron had assumed a light straw tint. Clearly, therefore, the process is one of direct oxidation of the metal, and thereby differs from ordinary rusting, which characterizes iron at lower temperatures in moist atmospheres. If the temperature of the metal is raised to that of dull redness (625-650° C.) the layer of oxide becomes sufficiently thick to admit of detachment with a knife. It is then observed to be a brittle mass, the composition of which is usually represented by the formula, Fe_3O_4. According to Mosander,[2] however, this is only true for the outermost layers of thick films formed at high temperatures, those layers nearer the metal having the formula $Fe_2O_3 . 6FeO$, that is, $Fe_3O_4 . 5FeO$. It does not follow, however, that this complex is a definite compound. It may mean that the first oxidation product of iron is ferrous oxide, FeO, which by further oxidation yields a skin of ferroso-ferric oxide, Fe_3O_4, upon its surface, which preserves to a large extent the under layers of ferrous oxide from further attack. Such a view is quite in harmony with our knowledge of the oxidation of iron and indeed of other metals in general.

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[1] Friend, "J. Iron Steel Inst." 1909, II, 172.

[2] Mosander, "Pogg. Ann." 1826, 6, 35.

(*b*) ACTION OF PURE WATER UPON IRON.

In summing up the knowledge of the reactions of iron as disseminated throughout the literature of his day, Robert Mallet[1] pointed out that pure air free water has no action upon iron at temperatures below its boiling-point, and quoted as his authorities, Hall,[2] Karsten,[3] and Westrumb. Perzoz[4] evidently shared the same view. A few years later, namely in 1845, Adie[5] showed that iron might be kept in water, entirely free from dissolved air, for a period of six months without exhibiting the slightest alteration in appearance. Quite recently, however, a new interest has attached itself to this question and a number of investigators have attacked the problem afresh, but with doubtful success.

The first of these was Whitney,[6] who immersed a piece of iron in boiling distilled water contained in a glass flask which had been previously well steamed out to remove any traces of soluble alkali. A rubber stopper, bearing a glass tube ending in a capillary, was inserted in the mouth of the flask, and, whilst the water was still boiling, the capillary was sealed by the blowpipe. On cooling, the stopper was well paraffined, and the entrance of oxygen and carbon di-oxide thus prevented. Flasks sealed in this way could be kept indefinitely without the iron undergoing any apparent change. In some cases a little air was admitted to the flasks, and within a few minutes the water became cloudy, rust being deposited both upon the glass and in spots upon the metal. Whitney, therefore, argued that, owing to the rapidity of the formation of oxide on admitting the air, a portion of the metal must have previously passed into solution, the air simply serving to precipitate out the insoluble rust. In support of this contention he cited an experiment carried out by J. A. Collins[1] in 1898, who took a clean iron pipe, 0·5 inches in diameter and 15 inches long, sealed at one end and fitted with a screw cap at the other. The tube was filled with boiling distilled water and the ebullition continued until half the water had boiled away. The cap was now screwed on and the temperature raised for an hour to 125° C. On cooling and pouring out of the pipe into a glass vessel, the water was seen to be perfectly clear and colourless, but on exposure to air a deposit of rust soon separated out. These results show very clearly that ordinary water can, under the particular conditions described above, dissolve small portions of ordinary iron. It would be unwise to push our conclusions further than this. Whitney gives no analysis of the metal used by Collins, and not having been able to secure an original copy of the thesis, it is impossible to say to what extent the solubility of the iron may have been influenced by the presence of non-metallic impurities such as sulphur and phosphorus. These elements are very liable to undergo reduction or oxidation, as the case may be, when in contact with hot water under pressure, particularly when the iron in which they are present is rich in occluded oxygen, or in particles of oxide distributed throughout its mass. The experimental data are thus seen to be insufficient to enable us to say with certainty that pure iron is capable of dissolving in pure water.

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[1] R. Mallet, "British Association Reports," 1838, p. 253.

[2] Hall, "Phil. Trans." 1818.

[3] Karsten, "Chim. du Fer."

[4] Perzoz, "Ann. Chim. Phys." (3) **24**, 506.

[5] Adie, "Min. Proc. Inst. Civil Engineers," 1845, **4**, 323.

[6] Whitney, "J. Amer. Chem. Soc." 1903, **25**, 394.

On repeating Whitney's own experiment two years later, Dunstan, Jowett, and Goulding[2] were unable to confirm his results, for, although the water in which the iron was boiled was tested by means of the exceedingly delicate thiocyanate reaction, not the least trace of iron could be detected in solution. In 1907, however, the whole question was thoroughly investigated by W. H. Walker, Cederholm, and Bent.[3] A round-bottomed Jena flask of about one litre capacity was inverted on a nozzle supplying live steam for at least twenty-four hours, thus ensuring the removal of any easily soluble alkalies which might otherwise have destroyed the neutrality of the water in the course of the experiment. A carefully cleaned rubber stopper was fitted to the flask in the manner described by Whitney. The flask was three quarters filled with ordinary distilled water, which had previously been boiled several hours in a block tin heater. After boiling for about ten minutes the stopper was removed to allow of the insertion of a piece of bright iron. It was then replaced, boiling continued for another ten minutes, and the capillary sealed. On cooling and coating with paraffin no change in the iron could be observed, but on opening and concentrating the water in a platinum dish, with every precaution to prevent contamination with dust, iron could always be detected in solution by the addition of potassium ferrocyanide, or thiocyanate.

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[1] Published in a thesis presented by J. A. Collins to the Massachusetts Institute of Technology in 1898.

[2] W. R. Dunstan, Jowett, and Goulding, "Trans. Chem. Soc." 1905, 87, 1557.

[3] Walker, Cederholm, and Bent, "J. Amer. Chem. Soc." 1907, **29**, 1251.

Thinking that possibly enough gas had been occluded to effect the reaction, the experiment was repeated, using iron which had previously been heated to dull redness and cooled in hydrogen gas. The same result, however, was invariably obtained. Finally, the water in which the iron was boiled was kept before use for a number of days over spongy metallic iron in order to remove every trace of oxygen. Introduction of this liquid into the reaction flask was effected by distillation from the spongy iron in an atmosphere of hydrogen. As blank experiments showed that no iron had dissolved from the glass walls of the containing vessels, the conclusion is drawn that iron is capable of solution to a minute extent in pure water, even in the absence of every trace of air or other gas, the failure on the part of Dunstan and his co-workers being attributable to the fact that they did not concentrate their water to a sufficient degree to arrive within the limits of sensitiveness of the tests employed. These results are further supported by Cushman[1] who has made a quantitative estimation of the solubility of iron in water. Six polished strips of metal 2·5 × 0·5 inches in area and 0·0625 inch in thickness were inserted into a flask containing 360 c.c. of boiling distilled water, and allowed to cool in complete absence of air. The liquid was then evaporated to dryness and ignited, the residual ferric oxide being weighed. This amounted to 0·0006 grm., equivalent to 0·00117 grm. of metallic iron per litre.

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[1] Allerton S. Cushman, "Bull. 30, U.S. Department of Agriculture," 1907.

There can be no doubt, therefore, that iron is slightly soluble in the purest water obtainable, in the complete absence of air, although for all practical purposes such solubility is negligible.

But the experiments of Walker and of Dunstan do not prove that iron is soluble in absolutely pure water, as Friend[1] has had occasion to show—and for the following reason. No fewer than seventy years ago Scoresby[2] was aware that air could never be completely removed from water by the mere process of boiling, for even after thorough treatment, air (gas) bubbles always appear on freezing the water. In a very interesting series of investigations Leduc[3] has again brought this fact into prominence. He further calculates that at least 1 c.c. of gas remains behind in a litre of water even after thorough boiling. Since carbon dioxide is not only much more soluble than either oxygen or nitrogen, but also combines with water to form carbonic acid, it is not unreasonable to suppose that a considerable percentage of this residual gas is carbon dioxide. This would readily effect the solution of a trace of iron as ferrous carbonate, and although the quantity produced might well be too minute to allow of immediate detection by chemical means, its concentration can be greatly increased by evaporating to small bulk when the characteristic reactions for iron may be obtained. The results of Walker and of Cushman are thus capable of explanation without assuming the solubility of pure iron in perfectly pure water, and the whole question has yet to receive a thoroughly satisfactory answer. The solution of the problem is undoubtedly more of scientific interest than of direct practical importance; but it is none the less essential that we give it due consideration, for unless we are guided aright in theory, our advance in practice is liable to be slow and uncertain. The reason for dwelling on this particular point at length will be evident when we come on to consider the various theories of corrosion, for Whitney's Electrolytic Theory stands or falls with the solubility or otherwise of iron in perfectly pure water. As Whitney's theory is the only serious rival of the older Acid Theory of Corrosion, the importance of the problem to chemists will be at once evident, But perfectly pure water is a scientific curiosity, and the experiments detailed above prove conclusively that iron is soluble to a minute but definite extent in all ordinary grades of water. Its coefficient of solubility, however, is so small as to be entirely negligible for all practical purposes, provided air or free oxygen is excluded.

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[1] Friend, "J. Iron Steel Inst." 1908, II, 5; 1909, II, 257.

[2] Scoresby, quoted by Mallet, "British Association Reports," 1838, p. 286.

[3] Leduc, "Compt. rend." 1906, **142**, 149.

(*c*) ACTION OF MOIST GASES UPON IRON.

That air laden with moisture rapidly effects the corrosion of iron has been known for centuries, although the *modus operandi* was not until comparatively recently made clear. Numerous experiments had been performed by different investigators[1] illustrative of the fact that damp oxygen was essential to corrosion, and it appears to have been generally understood that liquid water was likewise a *sine qua non*. In 1905 Dunstan and his co-workers[2] undertook a thorough investigation of the whole question. Pieces of very pure iron containing 99·94 per cent of metal were cleaned and introduced into a series of glass tubes, which latter were now heated to redness, a current of pure hydrogen gas being passed through, to ensure the reduction of every trace of oxide, and the simultaneous expulsion of any occluded gas. On cooling, the tubes were exhausted by means of a Sprengel pump, and filled with different gases, some of which were dried by passage through phosphorus pentoxide, others being moistened by bubbling through air-free water. They were then sealed and placed in a thermostat maintained at 34° C. so that, by avoiding fluctuations in temperature, no liquid water would condense upon the metallic surfaces. A precisely similar set of tubes was prepared and allowed to remain at the ordinary temperature. The results of the two series of experiments were as follows:—

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[1] Payen, 1837; Mallet, 1838, 1840; Adie, 1845; Calvert, 1871; and many others more recently.

[2] Dunstan, Jowett, and Goulding, "Trans. Chem. Soc." 1905, **87**, 1557.

Gas.	Appearance of the Iron Kept:— 1. At Constant Temperature.	2. At Variable Temperature.
Dry oxygen	No visible action	No visible action
Dry carbon dioxide . . .	,,	,,
Moist oxygen	,,	Copious rusting
Moist oxygen and carbon dioxide	,,	,,
Moist carbon dioxide . . .	,,	No visible action

Clearly, therefore, it is not the water vapour in the atmosphere which, as such, stimulates the corrosion of iron. Rusting can only take place when that vapour condenses to form drops of liquid water. This is a point of no little importance in metallurgical museums, where large numbers of specimens of fractures of iron are exhibited, which cannot well be greased over. If the temperature of the air is never allowed to fall below the dew-point, and the specimens are initially free from rust, corrosion will not take place. This has been practically demonstrated in some of the London museums, where numerous specimens of iron have remained bright and free from rust for as many as twelve years.[1] We have here, also, a partial explanation for the interesting observation that busy iron does not rust so readily as idle metal exposed to similar influences.

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[1] See Howe, "Metallurgy of Steel," 2nd. ed. 1891, Vol. I, p. 96. New York.

For example, it is a matter of common knowledge that railway lines in constant use lose far less by corrosion than do the rails of sidings, in any given time. This is frequently explained as the result of vibration shaking off the porous rust[1] or breaking up points of potential difference on the surface of the metal.[2] No doubt these are important factors and exert due influence upon the rate of corrosion. The present author would suggest another auxiliary, but not alternative, explanation, namely that the rush of any train over the metals produces a sensible rise in temperature, and before this heat has been altogether dissipated it is renewed by the passage of a second train. The rails are thus maintained at a temperature slightly above that of their surroundings, with the result that liquid water has no good opportunities of condensing upon them, or, if once condensed, it is rapidly evaporated away again, and corrosion is retarded.

The protective action of thin films of grease upon iron surfaces will now be apparent. Although the grease is frequently permeable to air and water-vapour, it is not so to liquid water to the same extent. Consequently the surface of the metal does not come into direct contact with water, and remains free from rust, so long as the grease film is preserved intact.

(*d*) BEHAVIOUR OF IRON POWDER TOWARDS AIR AND WATER.

All the experiments hitherto considered have dealt with iron in its compact form. It is of interest, therefore, to inquire if the same laws apply to iron powder. Hall and Guibourt[3] appear to have been the first to study this problem, and Ramann[4] states that, in one experiment, 10 grms. of iron powder liberated 12 c.c. of hydrogen gas from water at the boiling-point in the course of one hour. He further remarks that if the iron powder is boiled with water for several days in a lass vessel, the latter becomes corroded. It was impossible to say, therefore, from these data to what extent the catalytic action of the glass may have assisted the decomposition of the water by the iron powder. In order to eliminate this source of error, Friend[1] introduced 10 grms. of Merck's purest iron powder into a copper vessel filled with boiling water. The powder was first washed with sodium hydroxide solution, and finally with warm, air-free distilled water, in order to remove any adhering gases. It was found that a steady stream of hydrogen escaped from the water, showing that, even under these conditions, the iron powder was chemically active. The rate at which the gas was evolved, however, was only one quarter of that observed when the copper vessel was replaced by a glass one, indicating that the glass does exert some influence upon the reaction. These results speak for themselves; they do not, however, afford any clue as to the action of perfectly pure water upon pure iron powder, as the reader cannot fail to see.

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[1] See p. 99. [2] See p. 247.

[3] Hall and Guibourt, "Gmelin-Kraut," III, 300.

[4] Ramann, "Ber." 1881, 14, 1433.

Iron powder in a very fine state of division, such as that obtained by the reduction of the oxalate in a current of hydrogen or coal gas at as low a temperature as possible, is pyrophoric in the cold,[2] but to what extent the moisture normally present in the atmosphere is responsible for this still remains uncertain.

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[1] Friend, "J. Iron Steel Inst." 1908, II, 5.

[2] This property may be made the subject of a pretty experiment. See "Chemical Lecture Experiments," by G. S. Newth. Longmans & Co., 1905, p. 176.

III.

THE ACTION OF STEAM UPON IRON.

FOR more than a century it has been known that, when steam acts upon iron at a high temperature, a chemical reaction takes place, resulting in the formation of an oxide, variously known as hammer scale, magnetic oxide, and ferroso-ferric oxide (Fe_3O_4), and the simultaneous liberation of free hydrogen gas. The equation usually given as representing this change is :—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

St. Claire Deville[1] appears to have been the first to study the reaction quantitatively, and the results of his classical researches are well worth our attention. Finely divided iron was placed in a porcelain tube maintained at the desired temperature in a furnace. One end of the tube was connected with a glass bulb filled with water and surrounded by ice, its vapour pressure being thus fixed at 4·6 mm. The other end of the tube was attached to a manometer, and an arrangement whereby the whole could be readily evacuated or filled with any gas at pleasure. It was found that for every temperature a certain maximum pressure of hydrogen could be obtained in equilibrium with the iron, its oxide, and steam. If this pressure was reduced by removal of a portion of the gas with the air pump, more steam decomposed with the production of a further quantity of magnetic oxide and hydrogen until equilibrium once more set in. If, on the other hand, the pressure of hydrogen was temporarily exceeded by the introduction of an excess of the gas, a corresponding amount of magnetic oxide underwent reduction, yielding free iron and steam, until the pressure of hydrogen was reduced to its equilibrium value. The reaction was thus proved to be reversible, and to follow the general Law of Mass Action,[1] and to be therefore more correctly represented by the scheme:—

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[1] Deville, "Annalen," 1871, **157**, 71; "Compt. rend." 1870, **70**, 1105, 1201; 1870, **71**, 30.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

The numerical results obtained by Deville are given in the following table:—

Temperature of iron. °C.	Pressure of Water Vapour. mm.	Pressure of Hydrogen. mm.
200	4·6	95·9
265	4·6	64·2
360	4·6	40·4
440	4·6	25·8
860	4·6	12·8
1040	4·6	9·2
1600 [2]	4·6	5·1

An experiment was tried at 150° C., and the iron was decidedly attacked, but the reaction was so slow that accurate measurements were impossible. At 200° C. equilibrium was attained only after several days and nights of continuous heating. At 860° C. less than one hour was required.

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[1] The Law of Mass Action had just been formulated by two Norwegian chemists, Guldberg and Waage, and published in a work entitled "Études sur les affinités Chimiques," which appeared at Christiania in 1867. It was translated into German by Abegg, being included in Ostwald's "Klassiker," No. 104. See also abstract in "J. prakt. Chem." 1879 (2) **19**, 69.

[2] Preuner ("Zeit. physikal. Chem." 1904, **47**, 392) gives good reason for believing that Deville had probably over-estimated this temperature. At 1300° C. Preuner's porcelain tube softened and caved inwards owing to the partial vacuum within. It is very unlikely, therefore, that Deville's tube would have withstood a similar difference in pressure at a temperature of no fewer than 300 degrees higher. Possibly 1200° C. is nearer the mark than 1600° C.

It is interesting to note that, as the temperature rises, the equilibrium pressure of hydrogen becomes increasingly less. We must, therefore, ultimately arrive at a point when the pressure becomes practically nil, that is to say, at such a temperature the steam will have no action upon iron. We shall have occasion to refer to this again presently.

Within more recent years Preuner[1] has confirmed and, in some directions, extended Deville's work. The essential parts of his apparatus are shown diagrammatically in Fig. 2, but the reader is referred to the original paper for minor details. In the bulk of the experiments iron foil was used, some 25 sq. cm. in superficial area. This was introduced into a porcelain tube AB, the two ends of which were connected with glass bulbs E and F, partially filled with water and themselves united by a long piece of pressure tubing HK. The middle portion of the porcelain tube was concentric with a slightly wider magnesia tube CD, which was wrapped round with a spiral of thin platinum wire and could thus be electrically heated to any desired temperature. The whole was surrounded by the wider glass tube LM, and tightly packed with asbestos, which proved so thoroughly fireproof, that even when the magnesia tube was heated to 1000° C. and upwards for several hours, the india-

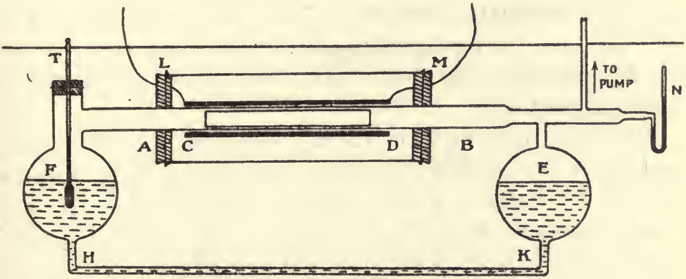

FIGURE 2.—APPARATUS USED BY PREUNER.

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[1] Preuner, "Zeit. physikal. Chem." 1904, 47, 385.

rubber stoppers L and M were only slightly attacked. The temperature of the water was given by thermometer T, from which the pressure of the water vapour in the apparatus was readily determined. By means of a thermo-electric couple (not shown in the Fig.) the temperature of the iron was registered, and the total gaseous pressure within the apparatus was given by the manometer N. In order to avoid any inequalities in the temperature, and particularly those errors caused by diffusion through the joints and walls of the containing vessels, the whole was immersed in a large water-bath.

After evacuating the whole apparatus, the porcelain tube was raised to the desired temperature, and, when equilibrium had been attained, the total gaseous pressure was observed. Knowing the pressure of the water vapour, that of the hydrogen was readily ascertained.

The range of temperature through which the iron was heated was not so large as that in Deville's experiments, being confined to 900° C., 1050° C., and 1150° C. respectively. But the pressure of water vapour in the apparatus was varied far more than it was possible for Deville to do with his arrangement, and the actual results obtained are more reliable, showing, in fact, a remarkable concordance amongst themselves. This reflects the very highest credit upon the author, G. Preuner, for the whole problem is beset by unusual experimental difficulty, as the reader who takes the trouble to refer to the original memoir, cannot fail to realize. Preuner's results are given in brief in the following table, and in order to render the figures comparable at the different temperatures, the pressures of hydrogen have been calculated[1] by both inter- and extra-polation whenever necessary. These calculated data, however, are enclosed in brackets, and may thus be readily distinguished.

It will be observed that, as the temperature of the iron increases, the equilibrium pressure of hydrogen always decreases, provided the pressure of aqueous vapour remains the same.

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[1] [By the present Author.]

Pressures of Hydrogen and Water Vapour in Equilibrium with Iron.

Pressure of Water Vapour. mm.	Pressure of Hydrogen in mm. in contact with Iron at:—		
	900° C.	1050° C.	1150° C.
10·0	14·2	—	(11·4)
11·5	17·9	—	(13·3)
17·4	26·0	(21·7)	19·9
25·1	37·4	(32·2)	30·4
35·4	54·1	(46·0)	41·1
40·9	(60·7)	53·9	(48·5)
44·9	(66·2)	57·9	(53·0)
49·3	71·8	(62·3)	58·2

This, it will be remembered, is in accordance with the observations of Deville. A series of curves may be drawn, one for each pressure of water vapour, representing the variation in hydrogen pressure corresponding to the different iron temperatures, the latter serving as abscissæ. It will then be observed that each curve, on prolongation, cuts the abscissa at a point corresponding to a temperature of approximately 2300° C. as shown in Fig. 3. At this temperature, therefore, steam would have no action upon iron, that is to say, the dissociation pressure of the iron oxide would equal that of the steam. Above 2300° C. the pressure of hydrogen would be negative, in other

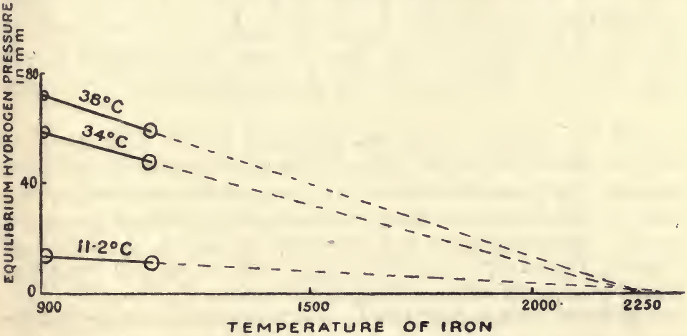

Figure 3.—Curve Illustrating Preuner's Results.

words any iron oxide would be reduced by the steam to metallic iron.[1] Possibly, however, such a condition of affairs could never be experimentally realized. It is unfortunate that Preuner was unable to study the reaction for a greater variety of iron temperatures. Like Deville, however, he found that, at 800° C. and below, the velocity of reaction was excessively slow, and thereby rendered accurate measurement a matter of no small difficulty;[2] on the other hand higher temperatures than 1150° C. could not be conveniently employed owing to the softening and consequent yielding of the porcelain tube. Had a greater range been practicable, however, it is quite possible that the curves shown in Fig. 3 would not have been so straight, but have curved inwards and, as the temperature advanced, have run asymptotically to the abscissæ. In this case, although the action of steam on iron at very high temperatures might be so small as to be negligible, the steam could never act as a reducer of iron oxide.

The determination of this upper limit to the action of steam upon iron has hitherto proved too difficult for practical realization. Friend, however, has sought for the lowest temperature at which any action becomes perceptible. Mallet[3] seems to have been aware, three quarters of a century ago, that steam had no visible action upon compact iron at 100° C. although it was well known to corrode the same at considerably higher temperatures. A series of preliminary experiments sufficed to show[1] that, whilst at 250° C. perfectly pure CO_2 free steam has no visible action upon pure iron foil, yet, when the temperature is raised to 400° C., a very marked corrosive action can be observed.

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[1] It is interesting to note, in this connexion, that the exact reverse of this has been experimentally proved by the present author to be true for copper. This metal is unacted upon by steam at any temperature below 1000° C., and freshly formed cuprous oxide may be reduced to metallic copper at this temperature, or a little below, by its aid. At white heat, however, Regnault ("Ann. Chim. Phys." 1836 (2) **62,** 364) found that copper decomposed steam, yielding cuprous oxide and hydrogen.

[2] No doubt Preuner would find an even longer time necessary to attain to equilibrium than Deville, since he employed compact iron in the form of foil, whereas the latter investigator used iron powder, obtained by reducing the oxide, and this, of course, had an immensely greater superficial area per unit mass.

[3] Mallet, "British Association Reports," 1840, p. 229.

In order to determine within narrower limits the temperature at which this activity becomes evident, the apparatus shown in Fig. 4 was employed. The distilling flask A was filled with a solution of caustic potash, and immersed in an oil-bath steadily maintained at about 120° C., whereby a regular stream of pure CO_2 free steam was obtained. Strips of pure iron foil were placed in the horizontal silica tube CD, only such metal being used as had previously been heated to redness in vacuo to ensure the removal of, at any rate, the greater part of its occluded gases. To remove the air as completely as possible from A, the potash was kept vigorously boiling for an hour or so before the experiment proper was commenced. CD was now filled with dilute ammonium hydroxide, which served to expel all the air from the tube. Ordinary distilled water could not be used on account of the rapidity with which the silica attacked the iron. On connecting CD with the distilling flask, the steam rapidly expelled the ammonia and water, and immersion in the solder-bath already at the desired temperature served to vaporize any remaining liquid. At the end of the ex-

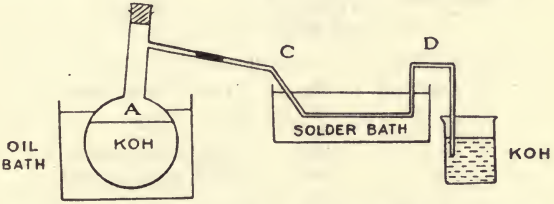

FIGURE 4. FRIEND'S APPARATUS FOR STUDYING THE ACTION OF STEAM ON IRON.

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[1] Friend, "J. Iron Steel Inst." 1909, II, 172; "J. West Scotland Iron Steel Inst." 1910.

periment, the bath was lowered and, after cooling to nearly 100° C., CD was rapidly disconnected and plunged into a bath of dilute potash solution. This served at once to cool the tube and to preserve the iron in contact with the silica. The metal was then removed and examined. The results of the experiments are given in the following table :—

THE ACTION OF STEAM UPON IRON.

Temperature. °C.	Duration of Experiment. (Minutes.)	Result.
295	60	Iron faintly attacked
330	60	,,
350	30	,,
350	60	Decided corrosion
385	60	Still more corrosion
430	30	,,

Now what interpretation are we to put upon these results? Is the faint corrosion observable at 295° C. to be attributed to the action of the steam or to the presence of air in the apparatus? Probably to the latter, for iron is readily attacked by air at 200° C. and above, as we have already seen in an earlier chapter, and the extreme difficulty of removing every trace of air from a piece of apparatus is fully realized only by those who have attempted the task. Further, at 330° C. with a temperature difference of 35°, the corrosive action is just the same. Since the traces of air remain practically constant in amount for any one apparatus, this is a result to be expected, unless the corrosive action were due to the steam, in which case, as the temperature increased, the action should have been more pronounced. At 350° C. very decided corrosion was observed after one hour, and as the temperature was raised the reaction became increasingly evident.

From these results Friend concludes that steam begins to decompose in the presence of iron at some temperature below

350° C. and that its action becomes clearly visible after one hour at 350° C. It is reasonable to suppose that no definite temperature could ever be fixed exactly at which the decomposition of the steam might be said to begin. For, at a certain temperature, the amount of decomposition which could take place might easily be so small as to elude detection in one hour, but yet in the course of several hours, days, or weeks, be most pronounced. Furthermore, the physical condition of the iron and of the walls of the containing vessels will probably exert a marked influence, for it is well known that gases are very susceptible to changes in these respects.

It was frequently observed that, on removing the iron from the silica tube at the conclusion of an experiment, very slight stains became rapidly darker in contact with the air, even though they were moistened with alkaline potash solution. Now pieces of iron coated with rust or with ferroso-ferric oxide may be kept for an indefinite time in contact with air and potash solution without the slightest change being observable. It seems reasonable to infer, therefore, that the darkening referred to is due to the presence of ferrous oxide which, in contact with oxygen, rapidly undergoes oxidation to a higher oxide. This would imply that the first product of the oxidation of iron in steam is ferrous oxide, and that this, as the temperature is raised or air is admitted, is further oxidized to ferroso-ferric oxide.

Friend next attempted to determine the lowest temperature at which free hydrogen could be detected in the steam after passage over pure iron. To this end the same apparatus was used, save that the evolved gases were collected in a eudiometer tube over potash, and the presence of hydrogen determined by explosion with excess of oxygen. Three grms. of iron foil were used in these experiments, having a total superficial area of 50 sq. cm. The results obtained are given in the following table :—

THE ACTION OF STEAM UPON IRON.

Temperature. °C.	Duration of Experiment. (Minutes.)	Volume of Hydrogen per Hour. c.cm.
318	120	0·00
332	120	0·00
340	120	trace
347	120	0·08
367	120	0·00
373	120	trace
408	120	0·44
456	120	1·00
410	50	5·16
570	10	18·0

Although traces of hydrogen could be detected at temperatures as low as 340° C., yet the amount of that gas was not appreciable until 400° C. had been attained. Above this temperature the evolution of hydrogen was very marked.

The fact that so little hydrogen could be detected at temperatures below 400° C. is easily explained. Although the foil was always corroded at about 350° C. and upwards, the action was very superficial, as the layer of oxide formed a protective coating to the underlying metal. Consequently the amount of hydrogen liberated was very small at first, and only became appreciable when the temperature was raised sufficiently to admit of deeper penetration by the steam.

It is evident, however, that both series of experiments agree in demonstrating the fact that pure steam has a detectable action upon pure compact iron at temperatures as low as 350° C., the probability being that the reaction begins at a considerably lower temperature still.

The usual explanation offered for the fact that iron is corroded by steam at high temperatures is that the iron itself decomposes the steam, uniting with the oxygen and liberating the hydrogen. This, however, is not easy to reconcile with the fact that hydrogen gas readily reduces the oxides of iron to the metallic condition—a reaction which is the direct reverse of that under discussion. Thus Glaser[1] finds that hydrogen reduces ferroso-ferric oxide at 305° C., and ferrous oxide at 370° C., whilst Hilpert[2] gives a lower temperature still for the reduction of ferrous oxide which has not been heated above 400° C., namely 280° C.

Friend suggests that the explanation for the corrosive action of steam on iron is to be found in the fact that the former is slightly dissociated into oxygen and hydrogen; the iron therefore combines with the free oxygen and allows the hydrogen to escape along with the undecomposed steam. The reaction, therefore, may be assumed to take place in three stages, comprising:—

1. The dissociation of the steam,

$$H_2O \rightleftharpoons H_2 + O.$$

2. The combination of the nascent, dissociated oxygen with the iron to form ferrous oxide,

$$Fe + O \rightleftharpoons FeO.$$

3. The further oxidation of the ferrous oxide to ferroso-ferric oxide,

$$3FeO + O \rightleftharpoons Fe_3O_4.$$

Alfred Holt, Junr.,[3] has recently attempted to determine the lowest temperature at which the dissociation of steam becomes a measurable quantity. As a result he finds that very small volumes of electrolytic gas can be collected at 775° C., a fact which indicates that dissociation must begin at a considerably lower temperature. There can, therefore, be no objection to the assumption that at 350° C. steam is very slightly, though decidedly, dissociated. If, now, the pressure of the oxygen in equilibrium with the steam is ever so little greater than the dissociation pressure of any oxide of iron at the same temperature, oxidation of the metal will take place. Walden[4] has recently shown that at even 1350° C. the dissociation pressure of ferroso-ferric oxide is so excessively small as to elude detection. At lower temperatures it will be smaller still, and may well be of the same order as that of steam at 350° C. The dissociation pressure of ferrous oxide is likewise excessively small, so that, whichever oxide is formed, there is nothing to render Friend's dissociation theory of the corrosive action of steam untenable, and since it possesses several advantages over the usually accepted theory, it would appear to be nearer the truth.

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[1] F. Glaser, "Zeit. anorgan. Chem." 1903, **36**, 1.

[2] Hilpert, "Ber." 1909, **42**, 4575.

[3] A. Holt, Junr., "Philos. Mag." 1909, **17**, 715.

[4] Walden, "J. Amer. Chem. Soc." 1908, **30**, 1350.

A few preliminary experiments have been carried out with the object of determining the action of steam upon iron powder. In 1907 Birnie[1] drew attention to the fact that the passage of steam over powdered iron, gently warmed in a glass tube, forms an excellent method of obtaining small quantities of pure hydrogen for lecture demonstrations and small experimental purposes. Friend has endeavoured to determine the lowest temperature at which hydrogen could be detected in the steam which had passed over heated iron powder. It was to be expected that this temperature would be lower than that found with iron foil, owing to the enormously greater superficial area of the powder. On the other hand we must not overlook the fact that results obtained with powders are not strictly comparable with those yielded by the same metal in the compact form; for not only are powders remarkably susceptible to catalytic influences from their containing vessels, but they possess, in addition, peculiar properties by virtue of their capillary forces and surface tension. As iron powder contains a good deal of occluded gas,[2] the metal used was first of all heated to redness in a stream of pure hydrogen gas, to effect its complete reduction, and, whilst still hot, the containing tube was evacuated as completely as possible by means of a mercury Sprengel pump. On cooling, air was admitted, and the iron finely powdered in an agate mortar, after which it was introduced into a silica tube exactly similar to CD (Fig. 4) save that a

[1] Birnie, "Chem. Zentral." 1907, I, 1771.

[2] See F. Krafft, "Ber." 1909, **42**, 210.

number of small bulbs had been blown in its underside, and in these the iron powder rested, otherwise the passage of the steam would have blown it completely out of the tube.

As a result it was found that the temperature to which the iron had to be heated before a trace of hydrogen could be detected in the emergent steam varied with the state of division of the metal, the coarser the powder, the higher being the temperature—as we might expect. When the metal was powdered as finely as possible in the agate mortar, traces of hydrogen were liberated at 240° C., that is, some 100° lower than was found to be the case with compact iron.

The practical importance of all these results will be evident when we remember that the formation of magnetic oxide by the passage of steam over heated iron constitutes a practical method of preventing its corrosion. This is the principle of the Bower-Barff process, which has been altered and improved (?) by whole armies of patentees. It is beyond the scope of this work, however, to deal with the subject here, but the subjoined references may prove of use to the reader.[1]

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[1] J. Percy, "J. Iron Steel Inst." 1877, II, 456. Barff, Paper read before Society of Arts, Feb. 1877. Bower, "J. Iron Steel Inst." 1880, I, 235. H. Haupt, "American Manufacture and Iron World," 1888, **42**, No. I. Gesner, "J. Iron Steel Inst." 1890, II, 850. De Meritens, "Industries," 1890, **5**, 444. J. Forbes, "Proc. and Transactions of Nova Scotian Inst. of Science," I. 27. M. P. Wood, "J. Iron Steel Inst." 1894, II, 437. C. Platt. "Engineering and Mining J." 1892, **54**, 78.

IV.

THE VARIOUS THEORIES OF CORROSION.

No fewer than five theories have been advanced from time to time to account for the corrosion of iron, and these we may now pass on to consider.

1. *Simple Oxide Theory.*—At first the process of rusting was regarded as an ideal example of simple oxidation, such as we have already seen to obtain when iron is heated to 200° C. and upwards in dry air. This was soon negatived, however, by the discovery that the presence of liquid water was essential to corrosion, in addition to air or oxygen gas. This fact paved the way for:—

2. *The Acid Theory.*[1]—It is difficult to say who was the first to suggest that pure liquid water and oxygen are insufficient of themselves to effect the corrosion of iron, and that at least a trace of acid must be present. The honour, however, is usually bestowed upon Crace Calvert,[2] who based his opinion upon the results of the following experiments:—

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[1] Owing to the prevalence of carbon dioxide in nature, and the fact that so much natural corrosion of iron is attributable to its action, this theory has often been incorrectly styled the "carbonic acid theory of corrosion". This, however, would imply that carbonic acid is the only acid which could induce corrosion, whereas it should be well known that almost any acid capable of attacking iron is also effective. See Gerald T. Moody, "Nature," 7 March, 1907; Friend, "J. Iron Steel Inst." 1909, II, 258.

[2] Crace Calvert, Paper read before the Manchester Literary and Phil. Society, 24 Jan. 1871. "Chemical News," 1871, **23**, 98. See Friend, "Chemical News," 1911, **103**, 138, where the origin of the acid theory of corrosion is discussed. It is pointed out that Berzelius was aware that alkalies inhibit corrosion—a fact that was, until quite recently, regarded as positive proof of the correctness of the Acid Theory of Corrosion,—

Clean blades of iron and steel were introduced into a series of tubes and placed over mercury together with various gases. After four months the tubes were examined, the observations recorded being as follows:—

CALVERT'S OBSERVATIONS ON CORROSION.

No. of Experiment.	Gas Used.	Appearance of the Metal.
1	Dry oxygen.	No oxidation.
2	Damp oxygen.	In three experiments only one blade slightly oxidized.
3	Dry carbon dioxide.	No oxidation.
4	Damp carbon dioxide.	Slight appearance of a white precipitate of iron carbonate. Two only out of six experiments did not show this.
5	Dry carbon dioxide and oxygen.	No oxidation.
6	Damp carbon dioxide and oxygen.	Oxidation most rapid. Blade assumed a dark green colour, which then turned a brown ochre.
7	Dry oxygen and ammonia.	No oxidation.
8	Damp oxygen and ammonia.	No oxidation.

These results appear to show that in the absence of carbon dioxide no corrosion takes place. No particulars are given as to the temperature and the extent of saturation of the moist gases by water vapour, so that it is impossible to say if liquid water ever condensed upon the metal in the majority of the experiments. If it did not, the absence of rust formation in experiment 2 is easily understood. Calvert's experiments were therefore inconclusive, although for many years this was not realized.

In 1888 Crum Brown[1] summarized briefly the most impor-

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and it is argued that the theory was probably one of gradual development. Crace Calvert was probably the first to give clear expression to the same in a recognized scientific journal.

[1] Crum Brown, "J. Iron Steel Inst." 1888, II, 129.

tant facts then recorded on the corrosion of iron, and supported the current idea that the action was primarily the result of acid attack—the acid usually being carbonic. This united with the iron yielding a ferrous salt, namely $FeCO_3$, or perhaps the soluble ferrous hydrogen carbonate, $FeH_2(CO_3)_2$, and the hydrogen liberated combined with any dissolved oxygen yielding water. The oxygen of the air then converted the soluble iron salt into the hydrated oxide or rust, liberating carbon dioxide, which was now free to attack a fresh portion of iron. Clearly, therefore, a small amount of carbon dioxide in the presence of liquid water and oxygen could convert an indefinite amount of iron into rust. Crum Brown evidently based his assertions upon the well-known fact that alkalies inhibit the corrosion of iron, a property which was attributed to their neutralizing any traces of free acid.

There can be no doubt that, at the time when this acid theory was promulgated, chemists were of the opinion that the presence of *free* acid was essential to corrosion, whereas such is not the case, for faintly alkaline solutions of the mineral salts of the alkali metals, such as the sulphates and nitrates of sodium and potassium, readily promote the formation of rust.[1] Clearly, therefore, it is essential to recognize the fact that corrosion can take place in the presence of an acid, irrespective of whether that acid is free or combined, the assumption being that the formation of an iron salt precedes the precipitation of ordinary rust.

Until quite recently the acid theory of corrosion was accepted without challenge. In 1903, however, Whitney[2] proposed :—

3. *The Electrolytic Theory of corrosion*, according to which the presence of an acid is not necessary to effect the rusting of iron. Whitney regards the whole subject as an electrochemical one, the rate of corrosion being simply a function of electromotive force and resistance of circuit. Water is assumed to be an electrolyte, that is to say a small proportion of its molecules

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[1] See Chapter X., where this branch of our subject is fully discussed.

[2] Whitney, "J. Amer. Chem. Soc." 1903, **25**, 394.

are ionized, yielding equivalent amounts of hydrogen and hydroxyl ions. We may represent this condition of affairs by the following scheme, where N represents a large whole number of uncertain value:—

$$N(H_2O) \rightleftharpoons (N-1)\ H_2O + H^{\cdot} + OH'$$

We are not to suppose that the atoms of $H^{\cdot}$ and OH' exist, as such, dissolved in the remainder of the un-ionized water, for such cannot well be the case. They are assumed to exist as isolated units, but charged with electricity, the hydrogen bearing a single positive charge, and the hydroxyl group an equal and opposite negative charge. These charges are represented by the signs · and ′ respectively. If a strip of iron be now introduced into such a system, a minute quantity passes into solution with the formation of iron ions, an equivalent amount of hydrogen ions losing their electric charges, whereby they are converted into atoms, and are precipitated upon the surface of the metal as a thin film of free hydrogen gas. In solution, therefore, we have virtually ferrous hydroxide, as is evident from the following scheme:—

$$Fe + 2H^{\cdot} + 2.OH' \rightleftharpoons Fe^{\cdot\cdot} + 2.OH' + H_2$$

or, according to the usual Berzelian system of nomenclature,

$$Fe + 2H_2O \rightleftharpoons Fe\ (OH)_2 + H_2$$

In this way the limited solubility of pure iron in thoroughly well boiled distilled water is explained, although, as we have already seen (p. 16) another equally satisfactory explanation can be offered. It will be clear that, if oxygen be now introduced into the above system, two things may happen, namely:—

(1) The oxidation of the $Fe(OH)_2$ to the red hydrated ferric oxide, $Fe\ (OH)_3$, which is precipitated as rust, thus:—

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

and

(2) The oxidation and consequent removal of the hydrogen film on the surface of the metal.

These two changes, of course, disturb the equilibrium; more iron passes into solution with consequent precipitation of a further quantity of rust, and so on.

The power of sodium hydroxide and of alkalies generally to inhibit corrosion is attributed to the presence of so many hydroxyl ions causing a suppression of the aqueous ionization, in other words reducing the number of hydrogen ions, so that the equilibrium represented by the equation :—

$$N(H_2O) \rightleftharpoons (N-1)H_2O + H^{\cdot} + OH'$$

is pushed from right to left, the value for N being indefinitely increased.

This very attractive theory has rapidly gained acceptance during the past few years, and we shall have occasion to discuss it fully in the sequel.

4. *The Hydrogen Peroxide Theory.*—Dunstan, Jowett, and Goulding,[1] after a long series of experiments, have come to the conclusion that Whitney is correct in assuming that pure oxygen and liquid water alone are essential to the corrosion of iron, the presence of an acid being unnecessary. Their interpretation of this conclusion, however, is entirely different, being based upon the scheme of oxidation processes first promulgated by Traube, in 1885.[2] According to this theory, hydrogen peroxide is formed as an intermediate product during the formation of rust in the manner indicated by the following equations :—

$$Fe + OH_2 = FeO + 2H$$
$$2H + O_2 = H_2O_2$$
$$2FeO + H_2O_2 = Fe_2O_2.(OH)_2 \text{ (rust).}$$

It will be observed that two molecules of peroxide are formed during the oxidation of two atoms of iron to ferrous oxide, and that only one of the former is required to oxidize the two latter to rust. The excess of hydrogen peroxide now attacks any uncorroded iron yielding ferrous oxide and rust, in the following manner :—

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[1] Dunstan, Jowett, and Goulding, "Trans. Chem. Soc." 1905, **87**, 1548.

[2] Traube, "Ber." 1885, **18**, 1881.

$$Fe + H_2O_2 = FeO + H_2O$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2 \text{ (rust).}$$

The inhibitive action of alkalies and chromic acid is explained by their power of decomposing the hydrogen peroxide.

The theory would appear also to derive some support from the fact that, when zinc corrodes in air and water, the presence of traces of hydrogen peroxide can readily be detected. This is true also in the case of many other metals. In order to demonstrate this a series of metals was shaken up with dilute sulphuric acid and air, and the liquid so obtained tested for hydrogen peroxide by the addition of titanium sulphate. This is an extremely delicate reagent to use, as it gives a well defined yellow colour in the presence of the merest traces of peroxide. The observations made by Dunstan and his co-workers are given in the following table:—

Copper.—After forty-eight hours the liquid was of a faint blue colour, and gave a distinct reaction for hydrogen peroxide.

Mercury.—After two hours a distinct reaction for hydrogen peroxide.

Silver.—After twenty-four hours a trace of hydrogen peroxide was found.

Lead.—The liquid became milky at once and gave a well-marked reaction for hydrogen peroxide.

Bismuth.—A well-marked reaction for hydrogen peroxide.

Tin.—The reaction was not so clear as in the case of bismuth.

Zinc.—A well-marked reaction for hydrogen peroxide.

Iron.—Although examined from time to time, no hydrogen peroxide could be detected.

It is noteworthy that hydrogen peroxide could be detected in the case of all the metals save iron, but owing to the rapidity with which it is decomposed by that metal, Dunstan argues that failure to detect its presence does not necessarily exclude the possibility of its momentary formation.

Against this theory, however, a whole army of facts can be arrayed.

(1) Pure, neutral hydrogen peroxide in dilute solution has no visible action upon iron, although it is itself catalytically decomposed by the metal, as Moody[1] has clearly shown. The opposite result obtained by Dunstan is attributable to the fact that his peroxide was not perfectly pure. Consequently the second group of equations representing the corrosion of iron by the action of hydrogen peroxide alone cannot be correct.

(2) As we have already seen, twice as much hydrogen peroxide is produced during the initial oxidation of the iron to the ferrous condition as is required for its further oxidation to rust. Consequently at least traces of the peroxide ought to be detectable provided delicate reagents are employed. Such, however, is not the case, and the excessively sensitive photographic method employed by Dony and A. Dony[2] likewise gave negative results.

(3) We have already remarked that the power of caustic soda and chromic acid to inhibit corrosion is, according to the theory under discussion, attributable to their tendency to decompose hydrogen peroxide, and thus remove it from the sphere of action. Moody[3] has pointed out, however, that other substances, such as potassium iodide, which immediately destroy hydrogen peroxide, do not inhibit the rusting of iron—a fact that is fatal to the peroxide theory.

(4) Finally, Divers[4] has drawn attention to the error of assuming that, because such bodies as chromic acid and the alkalies destroy hydrogen peroxide, therefore they must of necessity prevent its formation. By way of illustration he quotes the case of ferrous sulphate which rapidly removes chlorine, but does not prevent its formation from manganese dioxide and hydrochloric acid.

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[1] Moody, "Proc. Chem. Soc." 1903, **19**, 240; "Trans. Chem. Soc." 1906, **89**, 729.

[2] Dony and A. Dony, "Chem. Zentral." 1906, II, 203; from Section I, Kongresses f. Chemie und Pharmacie in Luttich, Vol. XX.

[3] Moody, "Nature," 7 March, 1907.

[4] Divers, "Proc. Chem. Soc." 1905, **21**, 251.

The peroxide theory is thus seen to be untenable and will not be referred to again. At the same time it is very ingenious and suggestive and well worth due consideration.

(5) *The Biological Theory.*—Not a few biologists have held that the corrosion of iron may be explained on the assumption that lowly forms of life enter into the reactions. The case has been well summed up by H. Richardson[1] who writes: "The facts that oxygen, water, and carbon dioxide are necessary; that iron does not rust when immersed in boiling water and then sealed up; that certain solutions are said to inhibit rusting (e.g. potassium ferrocyanide, a poison), and that certain other solutions encourage rusting (e.g. ammonium chloride and perhaps sea water; compare the composition of plant-culture solutions); that iron is a constituent of chlorophyll, and that rusty nails sometimes cause blood poisoning; all these facts suggest a case for inquiry."

B. Schorler,[2] Beythien,[3] Adler,[4] and Raumer,[5] have drawn attention to an organism which lives by decomposing ferrous carbonate or organic ferrous salts, with the precipitation of rust. But so far as the present author is aware, no organism has been discovered which can feed upon metallic iron. Indeed, if one such were found, it would have to get the iron into solution by some, presumably acid, secretion, which brings us back to the acid theory of corrosion again. As we shall see later, animal and vegetable organisms can, by their numerous secretions, very materially assist the corrosion of iron, and in all cases in which large masses of iron are exposed to the disintegrating action of natural forces, this biological aspect of the problem may not be overlooked. But corrosion can take place in the entire absence of living organic matter with great ease. Thus, for example, a 10 per cent solution of potassium chloride in dilute caustic potash (say tenth normal) will readily effect the corrosion of iron immersed within it, when enclosed with a small quantity of air in sealed tubes. It is certain, however, that no organisms could live in such a mixture. Further, Friend,[1] plunged hermetically sealed tubes containing pure iron, boiled water, and air, into boiling water. After two hours, when it was certain that any bacteria must have been killed, the tubes were removed and cooled. In each case it was found that the iron had been attacked. After two or three days the corrosion had greatly increased, and small patches of green could be detected upon the surface of the iron. Clearly, therefore, the corrosion of iron is not prevented by the exclusion of bacteria.

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[1] H. Richardson, "Nature," 11 October, 1906.

[2] Schorler, "Centralblatt f. Bakter. u. Parasitenk." 1904, **12** (ii.), 681; 1905, **15** (ii.), 564.

[3] Beythien, "Zeit. Unters. Nahr. Genussm." 1905, **9**, 529.

[4] Adler, "Centralblatt f. Bakter. u. Parasitenk." 1904, **11** (ii.), 215.

[5] Raumer, "Zeit. anal. Chem." 1903; **42**, 590.

Summary.—From what has been said it is evident that there are only two theories of corrosion which require further attention here, namely, the acid and the electrolytic theories, the remaining three having already been proved inadequate. According to the electrolytic theory, the presence of pure oxygen and liquid water *alone* are essential to the formation of rust upon the surface of pure iron, whereas, according to the acid theory, these substances are not sufficient, a trace of acid to effect the solution of the iron being absolutely indispensable.

It might appear at first sight that to decide between the two theories would be a matter of great simplicity,[2] for the presence of an acid can readily be detected by means of certain reagents, such as litmus and methyl orange. But further consideration shows that such is not the case. It has already been pointed out that according to the acid theory, a single molecule of acid is sufficient to initiate the process of rusting, and certainly in practice a very small number would be able to produce a visible effect in a few hours. Remembering that several million molecules of an acid could be placed side by side in a line less than one centimetre in length, it will be clear that many millions of such molecules would be necessary to respond to a colour test gauged by the naked eye. Hence such a method breaks down at once.

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[1] Friend, "J. Iron Steel Inst." 1908, II, 23.

[2] Compare Friend, "J. Iron Steel Inst." 1909, II, 258.

There still remain, however, two methods by which a decision may be arrived at, as to which of the two theories is correct. These may be enumerated as follows:—

(1) The determination of the solubility or otherwise of pure iron in pure, air-free water. If iron is once proved to be capable of solution in absolutely pure water, the truth of Whitney's theory may be regarded as established. This, however, is a very difficult task, all ordinary methods of experiment yielding a doubtful answer, as we saw in Chapter II.

(2) By observation of the result of bringing pure oxygen, liquid water, and iron into contact. This task has been attempted by a whole army of investigators, and a consideration of their results is left for the succeeding chapter.

V.

IS AN ACID ESSENTIAL TO CORROSION?

We may now pass on to consider in detail the more important researches which have been carried out with the direct object of deciding whether or not the presence of at least traces of an acid is essential to corrosion. For the sake of convenience we shall deal with these as nearly as possible in chronological order.

The Experiments of Dunstan, Jowett, and Goulding.

In 1905 Dunstan, Jowett, and Goulding[1] published a most interesting paper giving the results of their careful investigation of the phenomena involved in the rusting of iron. In order to demonstrate the action of liquid water and oxygen upon iron, the apparatus figured below was employed. The metal used was exceedingly pure, analysis showing that it contained 99·94 per cent of metal. Its surface was thoroughly cleaned and polished, any trace of oxide being subsequently reduced in a current of hydrogen. It was then inserted in the tube A, which latter was attached to the rest of the apparatus by means of a rubber joint. At the beginning of the experiment hydrogen, carefully freed from carbon dioxide by passage through several wash-bottles and towers containing caustic potash, was passed through the distilling flask C, which contained water, lime, and potassium permanganate. About 100 c.c. of water were then distilled into the Wolfe bottle D, tap *b* being closed, and the remainder of the apparatus evacuated as completely as possible by means of a mercury pump. *a* was now closed and, on opening *b*, water saturated with hydrogen gas distilled over into A and completely covered the piece of iron. On closing *b* oxygen was admitted to the iron through *d*, after having been freed from carbon dioxide by passage through wash-bottles containing aqueous caustic potash and finally through towers of the solid alkali. The apparatus above *b* was again exhausted and a second time filled with oxygen.

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[1] Dunstan, Jowett, and Goulding, "Trans. Chem. Soc." 1905, **87**, 1548.

When the iron remained in contact with water saturated with hydrogen and in an atmosphere of the same gas, no visible action took place. On admitting the oxygen, however, action immediately began, a greenish colour being produced which rapidly changed to the characteristic ochre hue of rust. The action was frequently local in character, the colour appearing in patches, a peculiarity which Dunstan attributed to some irregularity in the physical condition of the metal rather than to the presence of slag or other foreign material, as the metal was extremely pure.

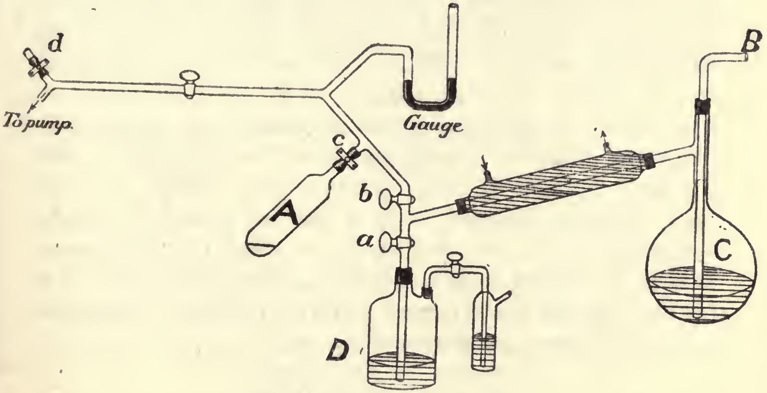

FIGURE 5.—DUNSTAN'S APPARATUS FOR SHOWING THE EFFECT OF LIQUID WATER AND AIR UPON IRON.

This experiment was repeated a number of times, and always with the same result, even when nitrogen was used in place of hydrogen. It seemed to be immaterial also whether or not light was excluded.

The authors, therefore, conclude that, *provided liquid water, oxygen, and iron are brought into contact, rusting will take place, even in the entire absence of carbonic and any other acid.*

Criticism.—A moment's consideration will serve to show that the precautions observed by Dunstan and his colleagues were not nearly sufficient to ensure the complete removal of all traces of carbon dioxide from their apparatus. During the past few years a number of investigators have demonstrated the extreme difficulty of removing the film of condensed gas to be found on every surface which has been exposed to the air for a time. Now glass apparatus is particularly liable to hold a layer of condensed carbon dioxide[1] on its inner surface, originating from the lungs of the glass blower who constructed the apparatus, and the mere precaution of exposing it to the poor vacuum, obtainable with a mercury pump at ordinary temperatures, is quite inadequate to effect its dislodgment. It is this residuum, small though it be, which might easily have initiated the process of rusting, and which renders it impossible to accept Dunstan's experiments as final.

CUSHMAN'S EXPERIMENTS.

Cushman[2] fitted up two Jena flasks as shown in Fig. 6, and filled them with freshly distilled water. The beaker C likewise contained distilled water, and this was raised to boiling in all three vessels. After the whole had been maintained in a state of vigorous ebullition for the space of half an hour, to ensure the expulsion of any traces of air, bright polished strips of charcoal iron were slipped into A, and the rubber stoppers, which had been previously cleaned by prolonged boiling in water, tightly inserted. After boiling for a further fifteen minutes clamp D was momentarily released, whereby a mixture of water and steam escaped with rapidity and expelled any traces of air from the tube. D was now closed again and the Bunsens removed from under A and B. As the steam in the flasks condensed, boiling water was sucked back from C until the apparatus was completely filled, no trace of air being present.

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[1] This is rendered all the more likely since carbon dioxide is a comparatively readily condensible gas, and we know that such gases are more easily attracted to surfaces than such refractory gases as oxygen and nitrogen.

[2] Cushman, "The Corrosion of Iron," Bulletin No. 30, U.S. Department of Agriculture. Washington, 1907.

It was found that the iron remained perfectly bright for an indefinite time in contact with this boiled, air-free water. Pure oxygen from a cylinder was now washed free from the last traces of carbonic acid by passage through a train of wash-bottles containing caustic potash, barium hydroxide, and lime-water. On allowing this to enter at D, and bubble through the system of flasks, rust appeared on the bright metal surfaces in the course of a very few minutes.

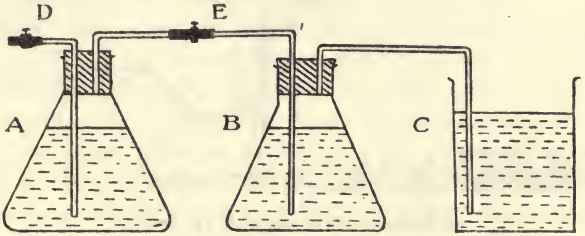

Figure 6.—Cushman's Apparatus to show the Action on Iron of Pure Water and Oxygen.

The action, just as in Dunstan's experiments, did not take place evenly all over the surface, but in patches which had the appearance of a more or less regular pattern, following the physical structure of the iron. As frequent repetition of the experiment never failed to yield the same results, Cushman concludes that "*carbonic acid is not necessarily present . . . before any reaction between iron, water, and oxygen, can take place*".

Criticism.—It has already been pointed out in Chapter II. that every trace of dissolved gas cannot be removed from a liquid by the simple process of boiling, however thoroughly and vigorously the ebullition is made to proceed. We are not justified, therefore, in assuming that rusting would take place on admission of pure oxygen, if these last traces of dissolved gas were removed. Cushman's experiments are thus seen to be indecisive as regards the point at issue, although they serve to show in the same way as those of Dunstan and his colleagues that, if acid *is* essential to corrosion, it need only be present in such inconceivably small amounts as have hitherto been regarded as quite negligible.

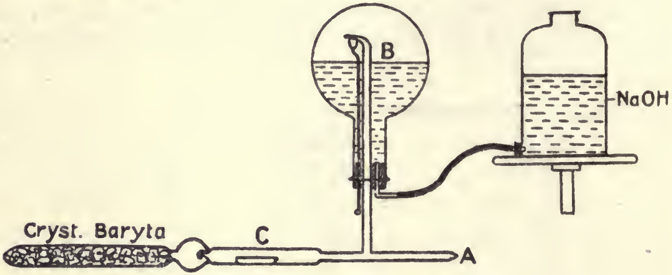

FIGURE 7.—TILDEN'S APPARATUS.

TILDEN'S EXPERIMENTS.

Tilden[1] employed the apparatus shown in Fig. 7. The metal used was Swedish soft iron in the form of rod some 6 mm. in diameter. It was entirely free from manganese and contained 0·103 per cent of carbon. A section prepared by Professor Gowland showed under a magnification of 3000 diameters the usual traces of slag disseminated throughout the mass. In order to avoid the disturbing influences inevitably caused by contact with glass, the iron, turned to a bright surface on the lathe, was placed in a silica boat and inserted in the horizontal tube. The capillary end of the vertical tube being sealed at B, the apparatus was connected at A with the mercury pump, exhausted as completely as possible, and the whole gently heated by a flame applied outside. In this way it was believed that any film of air adhering to the surfaces of the glass and metal would be removed. Connexion with the pump was then closed by the blow-pipe.

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[1] Tilden, "Trans. Chem. Soc." 1908, **93**, 1358.

B was now surrounded by a flask containing an aqueous solution of 5-normal caustic soda[1] connected with a reservoir. After oxygen, prepared from pure potassium chlorate, had been admitted into the flask, the whole was allowed to stand for three days in order to allow of the absorption of every trace of carbon dioxide in the gas. On breaking the end of the capillary by means of a wire, oxygen entered AB. The crystallized baryta was now heated, and, by surrounding C with ice, liquid water was made to condense upon the iron.

Rusting began in about ten minutes and proceeded rapidly. The experiment was repeated a number of times with slight variations, but the result was always the same. Tilden, therefore, expresses his conviction that "*commercial iron, liquid water, and oxygen are alone sufficient for the production of rust. Carbonic acid is not necessary, but when present hastens the action*".

Criticism.—Tilden's experiments are open to the same objection as are those of Dunstan, Jowett, and Goulding, in that the extreme difficulty of removing the layer of condensed gases to be found on the inside surfaces of all glass apparatus is not realized and allowed for. Tilden, it is true, warmed his apparatus when exhausted with a mercury pump, but even this precaution is far from sufficient to remove the last traces of the gas adhering to the glass, as chemists, and particularly physicists, are now learning. Again, the use of crystallized baryta as the source of pure water condensed upon the iron during the course of the experiment is unfortunate, for the same objections apply here as to Moody's employment of an aqueous solution of baryta for a similar purpose.[2] A third possible cause of the rusting observed by Tilden has been pointed out by Moody[3] who calls attention to the fact that commercial iron and steel invariably contain foreign substances such as sulphur and phosphorus. On exposure to air these readily oxidize with the production of acids, thus leading to the corrosion of the metal. Tilden's experiments cannot, therefore, be regarded as decisive.

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[1] That is, 200 grms. of NaOH per litre of solution.

[2] See p. 62.

[3] Moody, "Proc. Chem. Soc." 1909, **25**, 34.

The Experiments of Heyn and Bauer.

The apparatus used by Heyn and Bauer[1] is shown diagrammatically in Fig. 8. The experiments were carried out in 1903, but the results did not receive publication until 1908. A piece of iron foil M was suspended inside the glass cylinder Z, which at the beginning of the experiment was filled with air. The distilled water in F was now vigorously boiled, and a stream of CO_2- free hydrogen bubbled through BCF, tap H being closed. The hydrogen was obtained from a Kipp in the ordinary manner,

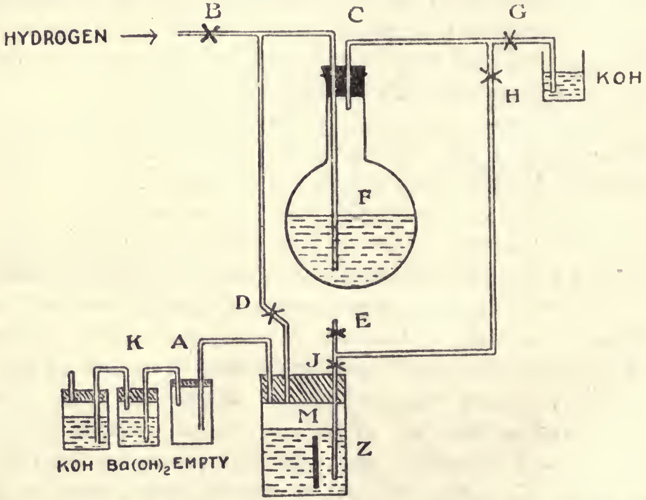

Figure 8.—Heyn and Bauer's Apparatus. (The crosses denote taps.)

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, 1908, **26**, 2.

and was purified by passage through wash-bottles containing aqueous solutions of potassium permanganate and caustic potash respectively. In this way it was believed that all traces of carbon dioxide would be expelled from the liquid and flask. The hydrogen gas was now made to pass through the remaining parts of the apparatus including the vessel Z, and to thus wash them free from adhering carbon dioxide. E was connected with an air supply, the air being freed from all traces of carbon dioxide, by passage through U-tubes filled with solid caustic soda, and wash-bottles containing aqueous solutions of caustic potash and barium hydroxide. On closing the taps B, G, and J, air was passed into EH, forcing some of the pure water through FCD into Z. D and H were now closed and J opened, so that air was compelled to pass into Z and escape through A. The apparatus was so entirely free from carbon dioxide gas that no trace of turbidity was observable in the baryta water in K. It mattered not whether the liquid in F consisted of Charlottenburg conductivity water or ordinary distilled water, the result was always the same, namely that the iron rusted in a very short time. It is therefore assumed that *liquid water and oxygen alone are sufficient to effect the corrosion of iron.*

Criticism.—These experiments of Heyn and Bauer are obviously open to the same objections as can be urged against those of the previous investigators, in that the extreme difficulty of removing the gaseous film adhering to the glass has not been realized and due precautions for its complete removal have consequently not been taken. These results, therefore, are not to be regarded as final, and will not be considered further.

MOODY'S EXPERIMENTS.

Probably the first person to realize the enormous difficulty of removing every trace of carbon dioxide from air and apparatus generally was Gerald T. Moody.[1] This investigator devised with remarkable ingenuity an apparatus in which small pieces of iron could be exposed to the combined action of pure air and water without the formation of rust. A distilling flask A, of capacity approximately 1500 c.c., was arranged in such a manner that its side tube passed through a long condenser case forming a bend at C in which the metal under experiment was placed. The other end of the bend was attached to a flask D, which acted as a receiver, and was itself connected in series with a large aspirator by means of a U-tube E, and potash tower F, the former being tightly packed with soda lime. On the posterior side of A was a second U-tube H also packed with soda lime and communicating with a caustic potash tower,[1] opening into an air reservoir[1] containing moistened sticks of caustic potash. When the aspirator was working, air entered the apparatus through a minute orifice at the upper part of the air reservoir. All parts of the apparatus between E and N were fused together so that leakage of carbon dioxide into the apparatus from the atmosphere was rendered practically impossible. All other joints were made with india-rubber pressure tubing, wired in position and covered with vaseline.

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[1] See Moody, "Trans. Chem. Soc." 1906, 89, 720.

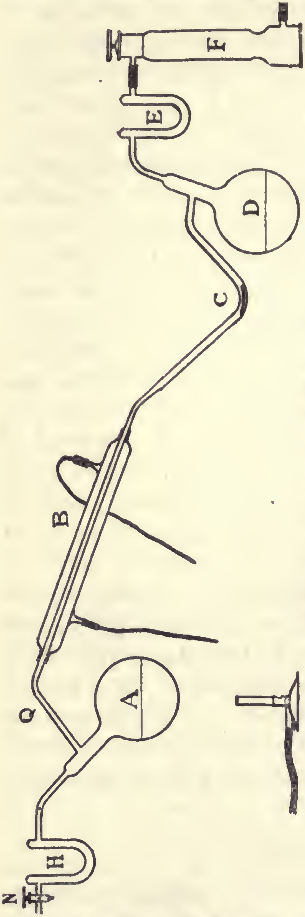

FIGURE 9.—MOODY'S APPARATUS.

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[1] Not shown in the figure.

The metal used was soft Swedish iron cut from a thick bar into cylindrical pieces, approximately 40 mm. long and 2 mm. in diameter. These were highly polished and slightly curved so as to lie evenly in the bent tube. The metal contained 99·8 per cent of iron and each cylindrical piece weighed a little less than 1 grm.

The experiment consisted in placing one of the pieces of iron in a bent piece of clean, dry, glass tube, which was as quickly as possible sealed into position at C. A slow current of air was drawn through the apparatus for about three weeks so as to remove all traces of carbon dioxide from contact with the iron. Water was now distilled from A, which contained a 1 per cent solution of barium hydroxide, until more than 500 c.c. had passed over. Tap N was closed during the distillation, and, with the object of preventing carbonic acid from finding its way into the apparatus through a sudden inrush of air, care was taken to cool very slowly at the completion of the process. A current of air was again drawn steadily through the apparatus and the metal kept under observation. The bent tube was of such a size and shape that each air-bubble, on passing through the water in it, brushed the upper surface of the iron, the lower surface remaining continually under water.

Under these conditions it was found that whilst the ends of the iron resting in contact with the glass always showed signs of corrosion in the course of a varying number of days, yet the surface of the iron was not generally rusted, a few brown specks merely making an appearance.

It appeared probable that this discoloration was due to carbonic acid and moisture shut in the apparatus during the process of fusing the bent tube C in its place, and accordingly a different mode of procedure was adopted. Before the bent tube was fused into position, it was partly filled with a 1 per cent solution of chromium trioxide, which just covered the iron. When the apparatus had been swept with air, free from carbon dioxide, for three weeks, water was distilled through the bend until all the chromic acid was washed into the receiver D. After the liquid in C became colourless the distillation was continued until a volume of water exceeding that already distilled had passed over. Air was again drawn through the apparatus, and at the end of six weeks the iron was perfectly bright, with the exception of those parts resting on the glass. These latter were slightly discoloured. As interaction between the glass and iron was clearly taking place, a means was devised whereby in subsequent experiments the contact between the two substances could be avoided. This was effected by covering the ends of the iron cylinders with paraffin wax. Commercial wax was purified by repeatedly shaking it, when molten, with hot water. On cooling to just above the melting-point, each end of the iron cylinder was repeatedly dipped in and out, whereby a blob of wax covering some 3 mm. of the metal was fixed at each end. The metal now lay inside the bent tube without touching the glass and the experiments were repeated as detailed above. In every case it was observed that, even after the long-continued passage of air through the water containing the iron, no corrosion took place. In one experiment the current of air was continued for no fewer than five weeks after distillation, during which period approximately 56 litres of air, containing practically 11 litres of oxygen, passed over the iron. Since the latter weighed but 0·9 grms., the total weight of oxygen exceeded, by thirty times, the amount required to convert the whole of the metal into ferric oxide. Not a single speck of rust appeared however.

In another experiment, after passing air, having a total volume of 32 litres, through the apparatus for three weeks, during which time the metal remained entirely free from corrosion, the glass tube was cut at Q, immediately above the distilling flask. Air, laden with the normal amount of carbon dioxide, but cleaned by passage through a tower containing pumice moistened with distilled water, was drawn through the apparatus. In the course of six hours the surface of the metal was distinctly tarnished. After seventy-two hours, during which time approximately 16 litres of air were drawn through, the whole of the metallic surface was corroded, and a considerable quantity of rust had collected in the bend of the tube.

Moody therefore draws the conclusion that "*when carbonic acid is entirely excluded, no interaction takes place between oxygen and iron in presence of water. Under such conditions, oxygen alone is unable to induce oxidation of the metal, but as soon as air containing its normal quantity of carbonic acid is admitted, vigorous rusting results.*"

Criticism.—These careful and ingenious experiments of Moody naturally attracted universal attention, and were provocative of a long and sometimes bitter controversy which has not yet been concluded. In order to give a clear and connected account of the various discussions on the subject, we shall do well to deal first of all with those experiments performed by Moody, without the employment of chromic acid, and secondly with those in which the iron was primarily immersed in chromic acid before being submitted to the combined action of pure air and water.

1. Those experiments in which chromic acid was not employed :—

Dunstan[1] has repeated Moody's experiments and, failing to obtain the same results, not unnaturally concludes that his own earlier work[2] thus receives confirmation. On the other hand Walker, Cederholm, and Bent,[3] on repeating Moody's experiments, obtained in general precisely similar results. Their explanation, however, is entirely different. Pure water is known to attack glass with ease, producing an alkaline solution which, although relatively weak in intensity, is sufficiently active to inhibit the rusting of iron. Moody's experiment was therefore again repeated in every detail, save that by a slight modification phenol phthalein could be introduced into the tube containing the iron and pure distilled water. The red colour, indicative of alkali, appeared in every case; but when air laden with carbon dioxide was bubbled through, the red colour gradually disappeared, an acid carbonate being formed accompanied by rapid corrosion of the metal. Jena glass tubes, which had been steamed out for two days to remove any soluble alkali, were then used in place of ordinary glass in constructing the apparatus. In this way the possibility that the distilled water surrounding the iron would contain any dissolved alkali was reduced to a minimum. As a result it was found that in every case the metal corroded almost as rapidly as when exposed to the open air. The conclusion, therefore, is drawn that in Moody's experiments it was the alkali dissolved out of the glass which inhibited the corrosion of the iron; and the fact, already alluded to, that Dunstan could not confirm Moody's results is attributed to his employing harder and less soluble glass than did the latter investigator. Moody, however, has proved to the present author that such an explanation is quite untenable. The glass tube used by him for containing the iron was boiled for a prolonged period with dilute acid and then for a still longer period with distilled water. The resulting tube gave neither an acid nor an alkaline reaction when left in contact with water for six weeks. Moody's experiments are thus seen to justify the conclusion that an acid is essential to corrosion.

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[1] Dunstan, "Proc. Chem. Soc." 1907, **23**, 63; "Nature," 21 February, 1907.

[2] *Vide supra*, p. 44.

[3] Walker, Cederholm, and Bent, "J. Amer. Chem. Soc." 1907, **29**, 1251.

2. Those experiments in which chromic acid was employed:—

Walker, Cederholm, and Bent point out that, since iron is rendered passive by immersion in chromic acid solutions, Moody's experiments in which this acid was employed simply show that passive iron is less easily corroded than ordinary active iron by the combined action of air and water.

Tilden[1] and Friend[2] have likewise drawn attention to the same point. Moody[3] in reply, however, argues that the true explanation of the effect of chromic acid is not that it renders the metal passive, but that it removes from the surface of the iron those constituents that would otherwise subsequently yield acids on exposure to water and oxygen. Further, H. B. Baker[1] has made many attempts to render iron indifferent towards ordinary water by treatment with dilute chromic acid solutions, but without success. Moody's view is no doubt true as far as it goes; but that iron is rendered passive by immersion in more concentrated aqueous solutions of chromic acid is also incontestible; and, whatever may be the ultimate cause of passivity,[2] there can be no reasonable doubt that the surface of the metal is then changed in relation to the liquid surrounding it. Consequently the resistance offered by such passive iron to corrosion is not strictly comparable with that of ordinary iron. Now it seems only reasonable to suppose that dilute solutions of chromic acid will exert the same kind of action on the iron as the stronger ones, although differing in intensity. Consequently chromated specimens of iron are to be viewed with suspicion for the purpose in hand. These experiments of Moody have, therefore, no direct bearing upon the point at issue and do not call for further consideration here.

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[1] Tilden, "Trans. Chem. Soc." 1908, **93**, 1356.

[2] Friend, "J. Iron Steel Inst." 1908, II, 12.

[3] Moody, "Proc. Chem. Soc." 1909, **25**, 34.

FRIEND'S EXPERIMENTS.

Friend has attacked the problem in a variety of ways, and in order to obtain a clear idea of the same we shall discuss each method separately.

Method 1.—This is identical in principle with that employed by Moody, differing from it only in a few minor details.[3] The results obtained by using pieces of iron and steel were confirmatory to those of Moody, who employed pure iron only. Cast iron, however, invariably rusted in the course of a few hours, as might be expected, since it contains numerous acid-forming impurities.

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[1] Baker, "Annual Reports of the Chemical Society," 1910, **7**, 38.

[2] See Chapter XII where the whole problem of passivity is discussed, particularly pp. 202-6, in which the action of chromic acid upon iron is considered in detail.

[3] Friend, "J. Iron Steel Inst." 1908, II, 16.

Method 2.—The principle of this method lies in distilling CO_2 free water on to iron in a hermetically sealed vessel containing perfectly pure air, and a glance at Fig. 10 will suffice to show the simplicity of the apparatus employed.[1]

A and B are two bulbs of 250 c.c. and 300 c.c. capacity respectively, blown in a hard glass from which pure water could dissolve no appreciable traces of alkali. A piece of iron and 100 c.c. of sodium hydroxide solution were introduced into B, and after the pressure of the air had been reduced to about 3 cm. of mercury, the vessel was hermetically sealed. The sodium hydroxide solution was prepared as free from carbonate as possible, by dissolving the requisite amount of Merck's purest hydroxide in freshly boiled distilled water. After shaking thoroughly and allowing to stand overnight in order to ensure the absorption of every trace of carbon dioxide from the air, walls of the vessel, and surface of the iron, the last-named was rinsed into A and the solution poured back into B. A was now kept cool either by a stream of cold water or by immersion in an ice-bath, whilst B was gently warmed in a hot-water bath. When about 60 c.c. of water had distilled into A, the hot-water bath was removed, and after shaking gently to wash the sides of A the liquid was poured back into B. By

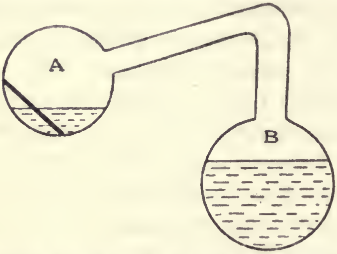

FIGURE 10.—FRIEND'S APPARATUS, ILLUSTRATING THE CORRECTNESS OF THE ACID THEORY OF CORROSION.

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[1] See Friend, op. cit. p. 13.

repeating this operation several times, pure water eventually collected in A. The vessel was then put in a quiet place in such a position that the iron rested with one-half immersed in the water, the remaining half being exposed to the air. At the end of a week or two it was found that the corners of the iron in contact with the glass had rusted very slightly owing to contact action with the silica. The surface of the metal, however, was unchanged, being as bright as ever, and exhibiting no sign of corrosion.

It was found, however, as the result of several experiments, that if very dilute sodium hydroxide solution was employed, for example, one-thirtieth normal (that is, 1·3 grm. per litre), the iron rapidly rusted not only at the corners in contact with the glass, but also on its surface. This result is of great interest theoretically, as we shall presently see.

The absence of rust in the experiments with normal and semi-normal caustic soda solutions might easily be attributed to the presence of alkali dissolved out of the glass, just as in Moody's and in Friend's previous experiments.[1] If such had been the case, however, the same source of alkalinity should have prevented corrosion in the otherwise precisely similar experiments in which one-thirtieth normal sodium hydroxide was used. But it did not, and the explanation is thus seen to be inadequate, and must be discarded. If, on the other hand, the acid theory of corrosion be accepted, a ready explanation is forthcoming. Since in making, filling, and sealing off the apparatus it was impossible to entirely exclude the presence of carbon dioxide, the sodium hydroxide solution was not absolutely pure, but contained traces of carbonate. For several years chemists have been familiar with the fact that solutions of sodium carbonate show signs of dissociation, and recently the reversible reaction represented by the equation:—

$$Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + CO_2$$

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[1] W. H. Walker, "J. Iron Steel Inst." 1909, I, 69; Friend, *ibid.* 1909, II, 257.

has been made the subject of careful inquiry.[1] Küster and Grüters,[2] have shown that the partial pressure of carbon dioxide in equilibrium with normal solutions of sodium carbonate is 0·000072 atmospheres at 90° C., and that the addition of a small quantity of caustic soda reduces this value very considerably. Since in the experiments with one-thirtieth normal sodium hydroxide, to which reference has been made, the sodium carbonate was not only present in small quantities but also in excess of sodium hydroxide, it is clear that the equilibrium pressure of carbon dioxide in the vessel must have been excessively small,[3] although a definite and decided amount. On the other hand, by using normal solutions the active mass of the sodium hydroxide is increased some thirty-fold, whereas the amount of sodium carbonate remains substantially the same. The equilibrium pressure of carbon dioxide is thus made vanishingly small. No doubt it is even then a definite quantity, and in the course of a few weeks or months it is quite possible that its action on the iron would be sufficiently pronounced to cause a visible amount of rust to form. If, however, its pressure were thereby reduced below that required for equilibrium with ferrous carbonate according to the equation

$$FeCO_3 + H_2 \rightleftharpoons Fe + CO_2 + H_2O$$

the iron would not rust at all.

A striking confirmation of the correctness of this line of argument has been afforded by the more recent experiments of Friend [4] which we may now pass on to consider.

Method 3.—The apparatus shown in Fig. 11 was employed. AE is a hollow cylinder of iron or steel, closed at one end.[5] The open end is plugged with a tightly fitting rubber stopper, bearing two glass tubes arranged in such a manner that cold water can circulate freely through them. The cylinder is well polished with sand-paper and secured inside a flask or bottle containing about 100 c.c. of twice normal caustic potash solution. The air is partly removed and the vessel hermetically sealed at F. The whole is now placed to about half its depth in a water-bath. After having been thoroughly shaken to remove every trace of carbon dioxide from the walls, air, and surface of the iron, a current of cold water is passed through AE, and the temperature of the bath raised to 100° C. The pressure of the air is not sufficiently reduced to allow the potash solution to boil, so that although pure water vapour condenses upon AE and drips off, there can be no spurting of alkali on to it. The metal is thus rapidly washed free from alkali, as may be demonstrated by opening the apparatus and testing with phenol phthalein, when no change in colour occurs. Nevertheless the iron remains perfectly bright for an indefinite number of days, thus demonstrating in a remarkably clear and decided manner that *pure water and pure air combined are without visible action upon pure iron.*[1]

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[1] McCoy, "Amer. Chem. J." 1903, **29**, 437.

[2] Küster and Grüters, "Ber." 1903, **36**, 748.

[3] But not so small, perhaps, as the results of Küster and Grüters would indicate, owing to the state of rarefaction of the air in the bulbs.

[4] Friend, "Proc. Chem. Soc." 1910, **26**, 179.

[5] An ordinary soda-water steel sparklet serves admirably, the neck having been filed off at a suitable place. This apparatus has now been placed on the market by Messrs. Philip Harris & Co., of Birmingham.

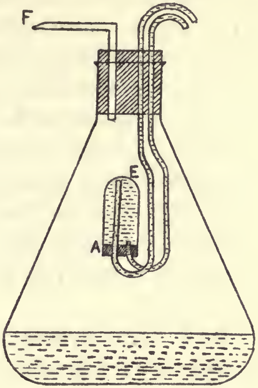

FIGURE 11.—FRIEND'S APPARATUS SHOWING THAT PURE AIR AND PURE LIQUID WATER CANNOT EFFECT THE CORROSION OF IRON.

The experiment was now repeated in every detail, save that the caustic potash was replaced by an equal amount of a saturated solution of barium hydroxide. Although in every other respect the experiments were precisely similar, the iron always rusted in the course of an hour or two. This shows that barium hydroxide is not sufficiently powerful to remove every trace of carbon dioxide from the air in the flask; in other words, its aqueous solution is in equilibrium with a definite, although minute, partial pressure of carbon dioxide. It is but fair to add, however, that the barium hydroxide was not specially purified, and no doubt contained an appreciable quantity of carbonate in addition to that formed from the carbon dioxide in the flask.

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[1] An isolated spot of rust will often form here and there upon the surface of the metal owing to the unavoidable traces of impurity always present in the purest metal obtainable, and if the apparatus is opened and the cylinder polished again with emery, the spots will appear again in the same places upon repetition of the experiment. Further, where the iron is in contact with the rubber a little corrosion takes place. These points, however, do not affect the general result of the experiment nor the legitimacy of the conclusions arrived at respecting the same.

As we have already seen, Moody employed aqueous barium hydroxide solution as his source of water, distilled on to the iron in his apparatus. Consequently unless the solution had been remarkably free from carbonate his metal must have rusted. Dr. Moody has kindly given the author, in a series of private communications, numerous unpublished details of his method of experiment, and there can be no doubt that the barium hydroxide, and the apparatus generally, were phenomenally free from all traces of carbon dioxide. Consequently the equilibrium pressure of carbon dioxide in the apparatus would be less than that required for corrosion. Had it been otherwise corrosion must have taken place. Herein possibly lies an explanation for the failure of Dunstan and of Walker, each working independently of the other, to confirm Moody's results, since these investigators may have unwittingly employed solutions less free from carbonate than did Moody.

THE EXPERIMENTS OF LAMBERT AND THOMSON.[1]

Lambert and Thomson [2] have prepared iron of extreme purity in the manner described below, and, on bringing this into contact with distilled water and pure oxygen obtained by the electrolysis of barium hydroxide, have observed that no rusting takes place.

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[1] These results were published in detail shortly after the present work was sent to the press, but through the kindness of Mr. Lambert, the author was permitted to see a private copy of the paper beforehand, from which the details contained in the above account have been culled.

[2] Lambert and Thomson, "Trans. Chem. Soc." 1910, 97, 2426.

The iron was prepared from Kahlbaum's pure ferric chloride by electrolysis of its aqueous solution in conductivity water between electrodes of pure iridium foil. This method is made practicable by the fact that pure iridium is not attacked by anodic chlorine. The metallic iron deposited upon the cathode was well washed and dissolved in dilute nitric acid and ferric nitrate crystallized out from the solution. After several recrystallizations the salt was obtained quite colourless, and was then transferred to an iridium boat and heated, whereby the oxide or basic nitrate resulted. The boat was now inserted in a silica tube and heated to bright redness in a current of pure hydrogen gas, obtained by the electrolysis of barium hydroxide.

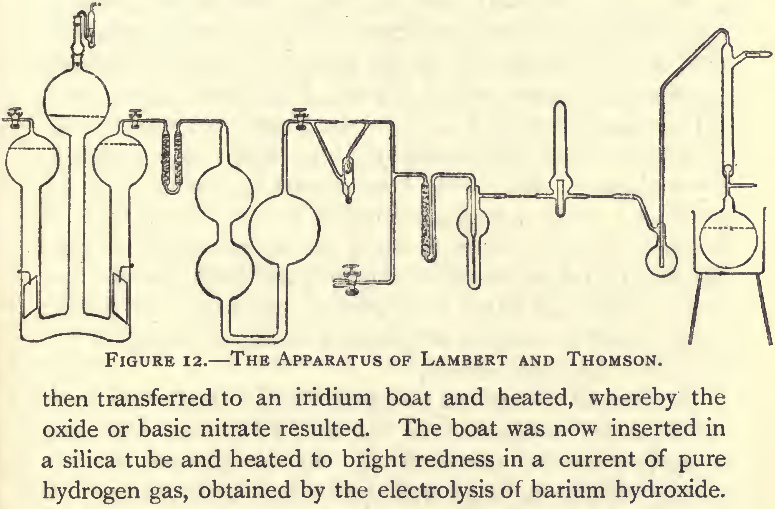

FIGURE 12.—THE APPARATUS OF LAMBERT AND THOMSON.

As prepared in this way the metallic iron had a distinct metallic lustre and a light grey colour. It was then transferred to a silica test-tube, maintained in a vertical position in the apparatus (Fig. 12), being supported by its lower end in such a manner that its open end and half its length were not in contact with the glass. The whole apparatus was then evacuated and pure water distilled from a dilute solution of barium hydroxide, contained in the flask on the right of the figure, some of it being condensed in a trap to prevent the possibility of any hydroxide being mechanically carried over to the iron. The liquid water which ultimately collected on the iron was thus perfectly free from alkali and had been condensed only on the walls of the silica test-tube. Oxygen was then admitted to the apparatus, being prepared by the electrolysis of barium hydroxide solution in a voltameter, as shown on the left of the figure, elaborate precautions being taken to effect the removal of any impurities which it might contain.

As a result it was found that the pure iron did not undergo any visible oxidation, there being no change even after several months. It was found, however, that, if ferric nitrate prepared from ordinary iron was used, even after repeated re-crystallization, for the preparation of the pure iron, rusting invariably occurred after a few hours. Further, if platinum vessels were used instead of iridium, in particular a platinum boat for the reduction of the ferric oxide, the iron invariably corroded at those places in which it had been heated in contact with the platinum. This is readily explained by the observations of Richards who, in his work upon the atomic weight of iron, employed platinum vessels throughout, and found that the iron always contained traces of this metal, and when dissolved in acids a small black speck of platinum invariably remained behind as an insoluble residue.

All kinds of commercial iron readily rusted under the same conditions of experiment, as did iron made with the most scrupulous care by other methods. Even a specimen of commercial electrolytic sheet iron, containing 99·9 per cent of metal, which had been polished and heated with a 1 per cent solution of chromic acid for three months, behaved in the same manner. The authors therefore conclude that *pure iron will not undergo visible oxidation in contact with pure water and pure oxygen, but that a small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions of experiment, even if this impurity be not of an acid nature or likely to produce an acid during the reaction.*

Criticism.—From what has preceded it will be evident that the precautions adopted are not nearly sufficient to ensure the complete removal of all traces of carbon dioxide from the walls of the apparatus. Furthermore the employment of a silica tube in which to contain the pure iron is open to criticism inasmuch as even silica is soluble in water, although to a very slight extent. Hence the corrosion of the less pure forms of iron observed by Lambert and Thomson was to be expected according to the acid theory of corrosion.

That the purest irons were not affected appreciably is a remarkable fact, and recalls the "noble" nature of pure zinc towards acid attack. Apparently, therefore, perfectly pure iron is indifferent towards the minute traces of acid which are so difficult to remove from an apparatus, or, at any rate, it is so slowly affected by them as to exhibit no appreciable corrosion in the course of a few weeks. These results, therefore, are in perfect harmony with the acid theory of corrosion.

CONCLUSION.

From the foregoing it will be evident that the most recent experimental results are entirely in favour of the acid theory of corrosion. But whilst we are thus bound to reject the electrolytic theory of corrosion, we are not to suppose that the electrolytic theory of ionization, as enunciated by Arrhenius, is likewise to be excluded in the explanations advanced to explain the various phenomena of corrosion; for the two theories are entirely distinct. It is through failure to distinguish between the "electrolytic theory of corrosion" in its restricted sense, and the "electrolytic theory" in its wider application, as referring to ionization generally,[1] that unfortunate misunderstandings have arisen. The general interpretation of corrosion phenomena will thus remain exactly the same whether the electrolytic or acid theory be accepted.

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[1] It is better, therefore, in the latter case, to use the term *ionic* theory, as this saves us from misunderstanding.

It may be well at this juncture to call attention to the fact that the electrolytic theory is based upon the assumption that water, even when perfectly pure, is ionized to a certain definite extent—an assumption for which we have no definite proof. Kohlrausch showed many years ago that water offers the greater resistance to the passage of an electric current the more carefully it is purified. A limiting value can, however, be reached, below which the conductivity cannot be reduced. Now, since we believe that the electric current is dependent upon ions for its transit through the liquid, it is argued that perfectly pure water contains a few ions. Kohlrausch and Heydweiller[1] distilled water repeatedly in platinum vessels in vacuo, and determined the conductivity as soon as the water was condensed. At 18° C. the value was $0{\cdot}0384 \times 10^{-6}$ ohms per centimetre, from which we calculate the ionic concentration to be $0{\cdot}78 \times 10^{-7}$ grm. ions per litre.[2] It is noteworthy that simple contact with air raised its conductivity tenfold in a very short time.[3] Now although this water was undoubtedly the purest that has ever been obtained in bulk, we have no proof that it was absolutely pure. Not a few chemists maintain that if absolutely pure water could be obtained, it would be found to be incapable of conducting an electric current—in other words, it would be entirely free from ionization. In an earlier chapter[4] we have considered the extreme difficulty of removing every trace of dissolved gases from water by boiling, and a very few molecules of carbon dioxide would be ample to give to an absolutely non-conducting specimen of water the minute conductivity observed by Kohlrausch and Heydweiller; so that their results may simply be a measure of the extent to which the dissolved gases remain in solution under the special conditions of the experiments. If such is really the case, the electrolytic theory of corrosion becomes a myth, whereas the acid theory is unaffected by it.[1]

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[1] Kohlrausch and Heydweiller, "Zeit. physikal. Chem." 1894, **14**, 317; "Wied. Annalen," 1894, **53**, 209.

[2] Nernst, "Theoretical Chemistry," translated by Lehfeldt. Macmillan & Co. 1904, p. 509.

[3] Kohlrausch, "Zeit. physikal. Chem." 1902, **42**, 193.

[4] See Chapter II.

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[1] Friend, "J. Iron Steel Inst." 1909, II, 257.

VI.

FACTORS INFLUENCING THE RATE OF CORROSION OF IRON EXPOSED TO NATURAL FORCES.

Iron and steel are usually regarded as very erratic in their behaviour towards corrosive agencies, and the explanation is not far to seek. The number of factors influencing the rate of corrosion is far greater than would appear at first sight, as no doubt a perusal of the next few pages will convince the reader who has not already devoted some time to their consideration. In the present chapter we shall confine ourselves to those factors which are likely to affect the corrosion of iron either totally or partially immersed in relatively pure natural waters and exposed to pure country air. This, of course, reduces the problem to its simplest form, and in succeeding chapters we can discuss the disturbing influences occasioned by the presence of dissolved salts in the water, of impurities in the metal, and the like.

The Quantity of Dissolved Oxygen in Water.

In the ordinary atmosphere the proportion of oxygen to nitrogen is approximately one volume of oxygen to four of nitrogen. If, however, air be shaken up with water, and the dissolved gases examined, the proportion of the gases is now found to be one of oxygen to two of nitrogen—a fact which it is not difficult to understand when we remember that oxygen is twice as soluble in pure water as nitrogen. Water, therefore, when saturated with air is an extremely powerful corrosive agent as regards iron and steel, and herein is to be found a partial explanation for the extreme activity of rain water and mist in effecting the oxidation of metals. It follows, therefore, that, if the amount of dissolved oxygen in boiler and tank water could be reduced by some chemical or physical means, the rate of corrosion of the metal would be reduced and its life proportionately prolonged. Now, freshly heated charcoal greedily absorbs gases of all kinds, a property which has been made use of practically by introducing charcoal as blocks or a coarse powder into drains, pantries, and the like. On account of its cheapness, therefore, charcoal would appear to be an ideal substance for the purpose in question. In order to settle this point by direct experiment, Heyn and Bauer[1] immersed a series of iron plates, measuring 4·5 × 3 cm. in area, in beakers of water, each vessel holding 250 c.c. of liquid and one plate only. The four corners of the metal touched the bottom and sides of the beakers and remained undisturbed in this position for a period of twelve days. The plates were then removed, cleaned, polished, and weighed, the loss in weight being taken as a measure of the corrosive action. Their results are given in the following table:—

RETARDING ACTION OF WOOD CHARCOAL ON THE CORROSION OF IRON.

Nature of Experiment.	Loss in Weight of Iron Plate in Grammes.[2] (Mean of Two Experiments.)	Relative Corrosion.
Distilled water only . . .	0·0377	100
A block of wood charcoal suspended in the water . .	0·0256	68
Powdered wood charcoal on surface of water	0·0077	20

The results are sufficiently striking to speak for themselves, and engineers would do well to give attention to the practical application of this method for the reduction of corrosion in boilers and water tanks generally.

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, 1908, **26**, 2.

[2] An analysis of the iron used in these experiments is given on p. 129.

Quite apart from any alkalinity which they may possess, the waters contained in the wells of the large gas-holders in our towns and cities will exert a smaller corrosive action upon the iron work more or less completely immersed in them, owing to their reduced oxygen content consequent upon saturation with coal gas. Friend immersed plates of iron, measuring 3 × 5 cm. in area, in 100 c.c. of fresh tap water and in a similar volume of tap water saturated with coal gas, in glass cylinders exposed to the air. After the lapse of eight days the plates were found to have corroded in the ratio of 100 to 86, showing that the influence of the hydrogen is very marked. In practical life this difference would be still more pronounced, for the waters remain saturated with coal gas during the whole of the time, whereas in the above experiment the hydrogen gradually diffused into the air.

River, stream, and well waters will naturally vary very much in their gaseous contents. Broad, deep, and sluggish rivers may be expected to contain less dissolved oxygen per unit volume of water, than the shallow stream which bounds from rock to rock and exposes a relatively enormous surface to the wind. Moisture, during its passage through the air as rain, absorbs large quantities of oxygen, and this must have no slight influence upon the amount of that gas present in our rivers during periods of flood caused by heavy falls of rain.

The enormous quantities of dissolved oxygen carried daily along by even our smaller rivers is scarcely realized by scientific men. On 8 December, 1910, the author, accompanied by Mr. Joseph Brown, measured the rate of flow of the river Tees near Darlington. This was found to be 2513 metres per hour. Samples of the river water were taken at the same time, and upon analysis were found to contain 8·1 c.c. of dissolved oxygen per litre, at N.T.P., from which it is calculated that more than 20 million c.c. of oxygen are swept past every square metre of cross section of the river per hour. If, now, a bridge be built over such a river supported by two central iron columns, 50 cm. in diameter, resting upon the river bed, and washed by the water to the modest height of 1 metre, these columns will together have a cross section of one square metre; and sufficient dissolved oxygen will be swept past them every hour to unite with 100 kilograms of iron to yield ordinary rust, and in twelve hours more than sufficient to corrode one ton of metal.

Where lakes are fed by mountain streams in showery districts, highly oxygenated waters result, and should these be particularly pure and free from dissolved mineral matter which might absorb or combine with the gas and thus reduce its amount, the waters will be unusually corrosive. This appears to be the case with Loch Katrine which, according to the analysis of a fair average sample, made by Professor Mills, contains 3·16 parts of solid in 100,000 parts. The waters contain about 3 cubic inches of dissolved oxygen per gallon, and Rowan[1] quotes some interesting cases illustrative of their unusually corrosive action on boilers, which caused the companies in question no little trouble and expense. It was observed, however, that boilers which had previously been fed with calcareous waters could afterwards be used with Loch Katrine water without suffering corrosion, and this was traced to the fact that a thin protective coating of lime had been formed within the boilers. The corrosion of the new boilers was then arrested by feeding regularly every morning for some time with a wash composed of Irish lime and water. The lime soon hardened under the influence of heat and no further trouble was experienced.

As is well known, rain water is particularly corrosive in its action towards iron, as Mallet[2] pointed out more than seventy years ago; and one of the chief reasons lies in the fact that it is not only very free from dissolved mineral matter, being, in fact distilled water of a high grade of purity, but during its passage through the air it has become saturated with oxygen. Another supplementary explanation is to be found in the fact that the air of our towns and cities is charged with oxides of sulphur and nitrogen which dissolve in the rain, rendering it either slightly acid, or charging it with varying amounts of soluble ammonium salts. It is well known, too, that after a thunder-storm, rain usually contains traces of ammonium nitrate in solution, even when in the country, situate leagues from a town or city. Such impurities as these greatly enhance the rate of corrosion, as we shall see in succeeding chapters. Their activity would be very limited, however, were it not for the abundance of dissolved oxygen which the rain water always contains.

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[1] Rowan, "British Association Reports," 1876.

[2] Mallet, "British Association Reports," 1838, p. 256.

THE AREA OF THE EXPOSED IRON.

In the case of iron articles partially or completely immersed in still water, the area of the metal exerts an irregular but important action upon its rate of corrosion. With our present experimental data it would appear that no general law can be formulated mathematically connecting the area and rate of corrosion, but it is universally found that the loss in weight experienced by a piece of iron immersed in water is not halved by halving the area,[1] that is to say, C is not proportional to A, where C represents the loss in weight, and A the area, other things of course being equal. The reason for this lies in the fact that iron, when once corrosion has set in, is capable of absorbing oxygen considerably more rapidly than the gas can be supplied to it by mere diffusion through the water. Consequently the concentration of the dissolved oxygen will be very low in the immediate neighbourhood of the metal, and gradually increase with the distance from it. Now it will be clear that, at points such as A and B on the perimeter of the plate, oxygen can diffuse towards the metal downwards, upwards, and sideways, as indicated by the arrows in Fig. 13, and corrosion will proceed most vigorously.

Towards all other points, however, oxygen can only diffuse in one direction, namely either straight down or straight up, according as the point lies upon the upper or under surface of the metal, and the rate of corrosion is proportionately reduced. The total corrosion, therefore, is the sum of these two unequal quantities, and may be represented by the equation :—

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[1] Unless, indeed, the water be very shallow.

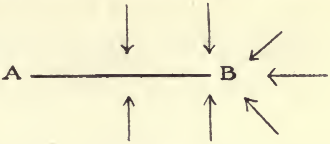

FIGURE 13.

$$C = P + S$$

where C, as before, represents the corrosion in toto, P that of the perimeter, and S that of the remaining surface.

Now in the case of all regular figures, such as circles and squares, quadrupling the area only effects a doubling of the perimeter. Consequently the corrosion of an iron plate of four times the area of the previous one would be represented by the equation :—

$$\begin{aligned} C^1 &= 2P + 4S \\ &= 4C - 2P \end{aligned}$$

from which it is evident that the corrosion is not four times as great. The same principle holds for all other shapes, but their mathematical expression is less easy than in the case of the circle and rectangle discussed.

This point has been demonstrated practically by Friend, who laid rectangular pieces of pure iron foil, of varying areas, upon a sheet of plate glass lying at the bottom of a large shallow trough, and covered them to a depth of 11 cm. with ordinary tap water. After a certain number of days the metal was removed, cleaned, and weighed, the results being as follows :—

THE EFFECT OF AREA UPON THE RATE OF CORROSION.

Time of Exposure. Days.	Area of Plate. Sq. cm.	Weight of Plate. Grm.	Loss in Weight per 100 sq. cm.	Relative Corrosion.
5	8	1·3726	0·0663	100
5	32	4·8790	0·0500	78
5	125	20·0700	0·0422	64
5	8	1·3620	0·0538	100
5	64	10·1740	0·0495	92
9	8	1·3534	0·1150	100
9	64	10·1116	0·1000	87

The question of the area of the metal is thus seen to be a very important one, particularly in carrying out test experiments in which it is essential that the conditions shall be as uniform as possible, and investigators must be careful to give due heed to this point, otherwise very conflicting results may be expected.

Closely connected with the above is the effect produced upon the rate of corrosion of iron immersed in water by the introduction of more pieces of iron in the immediate neighbourhood of, but not in actual contact with, the first piece. Here again no definite rules can be given, for experimental data on this point are lacking. But it is easy to see that the more numerous the pieces of iron the less will be the corrosion of each individual, other things of course being equal. The sum total of the corrosion, however, will be somewhat greater when all the pieces are immersed, than when only one or two of them are.

THE SUPERFICIAL AREA OF THE WATER.

In the case of iron articles completely immersed in still water, the surface of which is exposed to the atmosphere, the rate of corrosion will obviously bear some relation to the superficial area of the water. Thus, for example, an iron plate would corrode considerably more rapidly in vessel B (Fig. 14) than in vessel A, other things being equal. The reason is to be found in the fact that the extent of corrosion depends in this particular case almost entirely upon the rate at which oxygen can diffuse towards the metal, and this is determined by the area of the water to which oxygen has access. This has been practically demonstrated by Friend, who laid discs of pure iron foil, 7·5 cm. in diameter, in a series of circular glass dishes, with vertical sides, one disc lying in each vessel, and covered to a depth of 3 cm. with tap water. The internal diameter of the dishes was 8·5 cm., the superficial area of the water being in consequence 56·8 sq. cm. This, however, was reduced to varying quantities by floating upon the water discs of solid paraffin wax cut to exactly fit inside the dishes, each being bored with a hole in the centre, of varying diameter (see Fig. 15). After the lapse of five days the discs of iron were cleaned and weighed, the results obtained being given in the following table :—

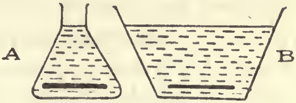

FIGURE 14.

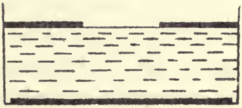

FIGURE 15.—EXPERIMENT TO SHOW THE EFFECT OF THE SUPERFICIAL AREA OF WATER UPON THE RATE OF CORROSION.

THE EFFECT OF THE SUPERFICIAL AREA OF WATER UPON THE RATE OF CORROSION.

Superficial Area of Water.	Weight of Iron.	Loss in Weight of Iron.	Relative Corrosion.
Sq. cm.	Grm.	Grm.	
56·8	7·9490	0·0382	100
12·6	7·9100	0·0220	58
0·8	7·8926	0·0052	14

These results speak for themselves, and clearly prove that the exposed area of the water has a marked influence upon the rate of corrosion. No definite mathematical expression can be drawn up, however, whereby the relationship between the two can be calculated, and the importance of giving due attention to this point in comparative tests of the relative corrodibilities of samples of metal is obvious.

Closely connected with the above is the action of an oily layer on the surface of the water. Owing to the fact that a thin layer of oil spread upon iron is an excellent safeguard against corrosion, it seems natural to conclude that, by pouring oil upon the surface of water in which iron is completely immersed, the same or at any rate analogous results might accrue. This, however, does not of necessity follow, for the two cases are quite distinct. In the former the protective action of the oil spread upon the metallic surface lies, not so much in its power of guarding the iron against contact with oxygen, as in its efficiency in preventing access of liquid water, the other essential to corrosion. In the arrangement under discussion, however, in which the oil film is floating upon the surface of the water, the latter liquid is already in contact with the metal and the effect of the oil depends upon its transparency to oxygen, that is to say, upon the ease with which it can absorb the gas and yield it up to the water beneath. The word transparency is used in this connexion, because it does not necessarily follow that an oil having a high oxygen coefficient of solubility will therefore part with a large amount of that gas when in contact with water. This is due to the fact that the solution of the oxygen is not always a physical one, as it is in the case of water. The so-called drying oils, for example, among which are classed such oils as linseed, tung, poppy, walnut, and hempseed, are capable of absorbing large quantities of oxygen, but the bulk of the gas enters into chemical combination with the oils, forming solid oxidation products which result in the well-known "setting" or "drying" phenomena.[1]

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[1] The term "drying" is a misnomer, and therefore unfortunate, as it implies that the oil loses water during the process, whereas water does not enter into the reaction at all.

In order to practically determine the effect of oil films upon the corrosion of iron in this way, Friend immersed weighed pieces of the metal in the form of foil, measuring 5 × 3½ sq. cm. in area, in a series of gas jars. Each jar contained one plate of iron and 100 c.c. of tap water, which in one series was fresh, whereas in the other it had been thoroughly well boiled to expel the dissolved air. 5 c.c. of three kinds of oil were now poured on to the surfaces of the water, one kind of oil, only, being added to each gas jar. The oils were linseed, olive, and paraffin—typical representatives of the three main classes of oil, namely, the drying oils, the fatty non-drying oils, and the hydrocarbon oils.

The first-named, that is, linseed oil, is an organic salt, being the glyceride of a group of fatty acids known under the generic name of linoleic acid. These acids are unsaturated and readily combine with oxygen to yield a tough, solid mass of uncertain composition, which goes by the name of linoxyn.[1] Linseed oil thus constitutes one of the best-known examples of the drying oils. According to the observation of W. Fox,[2] 5 c.c. of linseed oil can absorb approximately 1 litre (1000 c.c.) of oxygen gas. Olive oil is likewise a glyceride, the fatty acid content of which is oleic acid, which absorbs oxygen far less readily than the linoleic acids. Consequently olive oil is not a drying oil, 5 c.c. of it absorbing only about 50 c.c. of oxygen gas,[3] part of which is chemically combined, the remainder being merely physically held in solution.

The third oil, namely paraffin, is, like olive oil, no drier. It differs, however, from the two preceding oils in that it is not an organic salt, and consists of carbon and hydrogen only, for which reason it is classed by the chemist as a hydrocarbon. It is very permanent in the presence of air and water, the latter being unable to saponify it for obvious reasons. Consequently it forms an ideal substance for the lubrication of machinery[1] and any oxygen which it may absorb is held physically in solution. Although the solubility of oxygen in the paraffin oils naturally varies for different samples, we may take it that on the average 5 c.c. of the oil can absorb 1 c.c. of the gas, an approximation which is sufficiently near for our purpose.[2]

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[1] See "An Introduction to the Chemistry of Paints," by J. N. Friend. Longmans & Co., 1910, Chapters XIII and XVIII.

[2] W. Fox, "Oil and Colourman's Journal," 1884, p. 234.

[3] Fox, loc. cit.

After the lapse of eight days the plates of iron referred to above were removed, cleaned, and weighed, the following results being obtained :—

THE EFFECT OF OIL FILMS UPON THE RATE OF CORROSION OF IRON IMMERSED IN WATER.

Name of Oil.	Volume of Oxygen Absorbed by 5 c.c. of Oil.	Loss in Weight of Iron in Fresh Water.	Loss in Weight of Iron in Boiled Water.
	C.c.	Grm.	Grm.
No oil	0·2[3]	0·0266	0·0266
Paraffin	1	0·0222	0·0226
Olive	50	0·0195	0·0076
Linseed	1000	0·0092	0·0063

Evidently, therefore, although paraffin has such a low absorption coefficient for oxygen gas, it is very transparent to the same and affords but slight protection to the iron under the conditions described above. The protective action of the linseed oil, despite its great affinity for oxygen, is most pronounced. although even this oil is partially transparent to the gas.

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[1] See p. 175.

[2] St. Gniewosz and A. Walfisz, "Zeit. physikal. Chem." 1887, 1, 70.

[3] 5 c.c. of water absorb approximately 0·2 c.c. of oxygen at room temperature. All these numbers refer, however, to an atmosphere of pure oxygen in order to be comparable. In the ordinary air the first two values would be reduced to practically one-fifth, owing to the partial pressure of the oxygen being approximately one-fifth of an atmosphere. The values for the olive and linseed oils would remain much the same, as their absorbed oxygen is chemically united with the oil, and is thus an exception to Henry's Law.

It should be borne in mind, however, that these results apply only in the case of cold and neutral waters. Hot or alkaline waters are capable of attacking the fatty oils, decomposing them into glycerine and fatty acids, which latter readily attack iron and effect its rapid corrosion. This aspect of the problem, however, is dealt with in a succeeding chapter.[1]

THE DEPTH TO WHICH IRON IS IMMERSED IN WATER.

The depth to which an iron plate is immersed in still water exposed to the general atmosphere will greatly affect its rate of corrosion, for, when once it has used up the dissolved oxygen in its immediate neighbourhood, it is dependent for its further supply upon the rate at which fresh oxygen can diffuse towards it, and this will be all the more rapid the nearer the iron is to the surface.

This appears to have been first pointed out by Mallet,[2] and has been well demonstrated quite recently by the interesting researches of Heyn and Bauer[3] to which reference has already been frequently made. These experimenters suspended iron plates, measuring 4·5 × 3 cm. in area, by means of glass hooks, at various depths beneath the surface of water in a series of tall glass cylinders, as shown in Fig. 16. After varying intervals of time the loss in weight was determined, and taken as a direct measure of the corrosion that had taken place. The numerical results obtained are given in the following table:[4]—

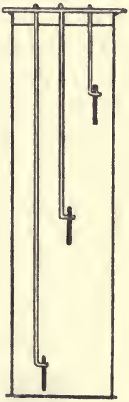

FIGURE 16.—EXPERIMENT TO ILLUSTRATE THE EFFECT OF DEPTH OF IMMERSION UPON THE RATE OF CORROSION.

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[1] See Chapter X.

[2] Mallet, "British Association Reports," 1840, p. 228.

[3] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1908, **26**, 14.

[4] An analysis of the iron used is given on p. 129.

THE EFFECT OF DEPTH OF IMMERSION UPON THE RATE OF CORROSION.

Depth of Immersion.	Loss in Weight of Iron After :—			
	8 Days.	15 Days.	22 Days.	29 Days.
Cm.	Grm.	Grm.	Grm.	Grm.
5	0·0268	0·0480	0·0731	0·0783
28	0·0244	0·0450	0·0628	0·0766
50	0·0206	0·0364	0·0606	0·0788

The results further show, however, contrary to expectation, that, as the time of exposure increases, the difference between the rates of corrosion at various depths becomes less pronounced. This is undoubtedly due to the fact that as the depth increased so did the proportion of ferrous oxide, so that for a given weight of oxygen more iron was attacked than was the case nearer to the surface, owing to the slow reduction of the rust first formed, according to the equation:

$$Fe + Fe_2O_3 = 3FeO$$ [1]

That such an action can take place may be readily seen by observing the corrosion of a piece of wire gauze pushed into a gas jar and, after soaking with water, inverting in a basin of the same (Fig. 17).

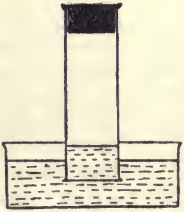

FIGURE 17.—THE CORROSION OF IRON GAUZE IN LIMITED AIR SUPPLY.

After a few hours the gauze is covered with ochre-coloured rust and the water rises up the gas jar indicating the absorption of oxygen. After a few days, however, the brown colour has entirely disappeared, the metal being now greenish in appearance, the rust having been reduced to ferrous oxide, more or less hydrated.

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[1] For the sake of clearness this equation is reduced to its simplest form, the presence of combined water in the rust being neglected, and also the traces of electrolyte, always present in natural waters, essential to corrosion.

It is quite possible, therefore, that when the time of exposure is still further increased, the extent of the corrosion of the lower plates will again become smaller, for, when all the brown ferric hydroxide is reduced to the ferrous condition, the metal not yet attacked becomes dependent upon diffused oxygen for the formation of even its ferrous oxide.[1]

The practical importance of these data is very great, and an explanation is thus afforded for the fact, well known to painters and structural engineers, that iron columns and beams are far less corroded when completely immersed in water at considerable depth, than when near to the surface where air can readily gain access. As we shall presently see, however, the rate of diffusion is not the only factor to be considered here, for the difference in the intensities of the light near the surface of the water and at greater depths exerts a marked influence.

THE PARTIAL PRESSURE OF OXYGEN.

Variations in the partial pressure of oxygen in contact with moist iron in the open have in general a relatively slight effect upon the rate of corrosion of the metal, provided extremes are avoided. This is because gases are continually moving, so that fresh portions are constantly swept across the surfaces of articles exposed to their action, diffusion and convection being the chief motive forces. In deep wells and the like, where the temperature is uniform and fresh air can rarely penetrate, the bulk of the oxygen would soon be absorbed by any iron, and further corrosion would be limited by the rate at which the remaining oxygen could diffuse towards the metal. This latter is particularly true also in those cases in which the metal is entirely immersed in water, for the solubility of oxygen in any liquid is dependent upon its pressure in the adjacent atmosphere. The rate of corrosion of the iron depending, as we have already seen, upon the solubility of oxygen in water, will therefore be largely affected by the partial pressure of that gas in contact with the water. This has been clearly demonstrated in a practical manner by Walker, Cederholm, and Bent,[1] who introduced weighed pieces of pure iron wire into Jena flasks partly filled with boiling water. On cooling, each flask was connected to a separate reservoir containing definitely known proportions of oxygen and nitrogen, and remained in this condition for five days. At the end of this period the metal was removed, cleaned, and weighed. The results are given in the following table :—

---

[1] This is, of course, assuming that the water is fairly pure, such as lake or river water, so that any galvanic action is slow and may be neglected. If it contain electrolytes in solution to any appreciable extent, fairly rapid galvanic action will set in owing to the difference of potential between the ferrous oxide and unattacked metal, whereby the whole problem becomes complicated. We shall refer to this galvanic action again in detail in Chapter XIV.

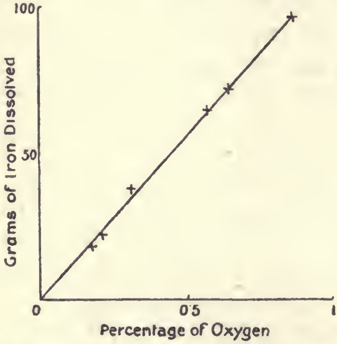

FIGURE 18.—CURVE SHOWING RELATION BETWEEN THE RATE OF CORROSION AND PARTIAL PRESSURE OF OXYGEN.

Percentage of Oxygen.	Loss in Weight of Iron.
18·2	0·018
21·8	0·021
28·0	0·031
64·5	0·057
72·1	0·064
97·0	0·086

In Fig. 18 the above results are shown graphically, and are sufficiently obvious to speak for themselves.

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[1] Walker, Cederholm, and Bent, " J. Amer. Chem. Soc." 1907, **29**, 1251.

In this connexion attention must be drawn to the researches of W. L. Dudley,[1] upon the effect of coal gas on the corrosion of wrought iron pipes buried in the earth. This investigator placed pieces of gas pipe, the ends of which were closed with corks and thickly paraffined over, into cubical wooden boxes containing various kinds of soil. The boxes were occasionally sprinkled with water, and after the lapse of twelve months the tubes were removed, cleaned, and weighed. A similar series of experiments was carried out in which the tubes were perforated with small holes, half a cubic foot of gas being passed daily through each tube into the soil in the boxes. The amount of corrosion which took place under these conditions was determined, in the previous series, by weighing. The results obtained are given in the following table :—

Sample of Earth.	Loss in Weight of Pipes.	
	Without Gas.	With Gas.
1. Taken from a street at the depth of the gas pipes	20·56	9·17
2. Taken from yellow clay, four feet below the surface in the city of Nashville . . .	13·53	6·34
3. Loamy clay, taken from just below the street electric car tracks	2·56	1·54
4. Clay from a vacant lot in the city . .	2·51	1·17

Whilst the method of experiment is open to many objections on account of its crude nature, the results are so striking as to far outweigh any error of manipulation, confirming the view that the partial pressure of the oxygen has, under these conditions of experiment, a great influence upon the rate of corrosion.

It will be clear, now, that one of the simplest methods of preserving iron articles consists in burying them in the soil at such depths that free oxygen can only diffuse with extreme slowness to them, and in such localities that no acids or acid salts can gain access to them.[1]

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[1] Dudley, "J. Amer. Chem. Soc." 1908, **30**, 247.

RATE OF MOTION OF THE WATER.

It is both interesting and instructive to try and gain an insight into the nature of the changes induced in the rate of corrosion of iron completely immersed in water, when the latter is agitated or made to flow in one direction or another.

When water is in motion, especially if it is shallow, it will always contain a fairly high percentage of dissolved oxygen, provided the atmosphere can gain access to its surface; and particularly is this the case when the surface of the water is ruffled by wind. Iron exposed to its action, therefore, is very liable to rapid corrosion, for fresh layers of the oxygenized water are continually replacing those which have been deprived of some or all of their gas by lying in contact with the iron. This is the condition of affairs which obtains in rivers and streams, and it is well known that metal columns dipping into these require careful attention. A very similar action to the above is afforded by the replacement of water in tanks and cisterns, both in private houses and in the large manufacturing establishments. Other things being equal the rate of corrosion will depend to a great extent upon the number of times that the tanks are re-filled, in other words, upon the amount of inflowing water. Water mains in our towns and cities are open to precisely the same action. This was well illustrated a few years ago by the investigations of Jamieson,[2] who pointed out that the corrosion in street water-main pipes is proportional to the amount of water passing through them, and quoted a case which had come under his own observation. One of the branches AC (Fig. 19) of a water main terminated in a closed end C. From A to B were about thirty branches drawing off a large supply of water, diminishing in quantity towards B. After having been in use for forty-five years, inspection showed that the pipe was almost choked with rust at A, but gradually cleared towards B. Between B and C, where the water had remained more or less stationary the whole of the time, practically no rust had accumulated.

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[1] It is here assumed that no stray electric currents are likely to occur, otherwise electrolysis will be set up resulting in rapid corrosion (see Chapter XIV).

[2] M. B. Jamieson, "Min. Proc. Inst. Civil Engineers," 1881, 65, 323.

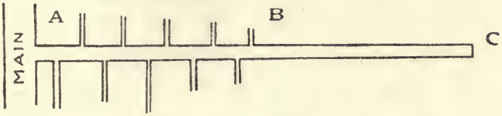

FIGURE 19.

Should the iron immersed in water contain hollows at its joints, as shown at A (Fig. 20), bubbles of air will collect in these, and corrosion proceed apace.

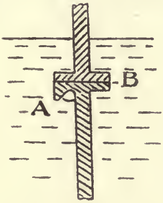

FIGURE 20.

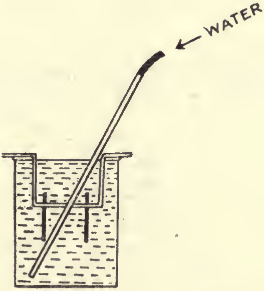

FIGURE 21.—HEYN AND BAUER'S APPARATUS DESIGNED TO SHOW THE EFFECT OF RATE OF FLOW OF WATER UPON CORROSION.

A very interesting series of investigations has recently been carried out by Heyn and Bauer[1] with the object of determining the effect produced by varying the rate of flow of water over the surface of iron plates. Two plates of steel, measuring 4·5 × 3 cm. in area, were suspended by means of a suitably bent glass rod within a beaker, as shown in Fig. 21, and covered with water, a uniform stream of which was continuously introduced through the delivery tube for a period of three weeks, the waste escaping over the edge of the beaker. Other precisely similar pieces of apparatus were constructed in which a different rate of flow of water was maintained, which, however, was constant for any one vessel. At the close of the experiment, the metals were removed, cleaned, and weighed, the results obtained being given in the following table, and shown graphically in the curve (Fig. 22). An exactly similar series was likewise carried out with cast-iron plates, the results of which are also embodied in the accompanying table and figure.

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1910, **28,** 93 *et seqq.*

THE EFFECT OF RATE OF FLOW OF WATER UPON THE CORROSION OF CAST IRON AND STEEL.

Cast Iron.			Steel.[1]		
Rate of Flow of Water in Litres per Hour.	Loss in Weight of Iron.[2]	Relative Corrosion.	Rate of Flow of Water in Litres per Hour.	Loss in Weight of Iron.[2]	Relative Corrosion.
	Grm.			Grm.	
0	0·0350	100	0	0·0566	100
6·6	0·2971	849	15	0·1357	240
36	0·2912	832	50	0·0826	146
240	0·1470	420	350	0·0377	67

The results are very striking, illustrating the fact that the rate of flow of the water exerts a remarkable influence upon the rate of corrosion. A gentle flow increases the corrosion to more than eight times the amount experienced when the liquid is at rest. Further increase in the rate of flow, however, causes a reduction in the corrosion, which latter is still, however, in the case of the cast iron, considerably greater than that taking place in the liquid at rest.

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[1] An analysis of this metal is given on p. 129.

[2] Average of the two suspended in each beaker.

THE EFFECT OF PARTIAL IMMERSION IN WATER.

It is a matter of common knowledge that iron always corrodes most rapidly when subjected to the alternate action of wet and dry. Such is the state of affairs at the water-line of iron ships, of bridge columns, and the like, and it is to these parts that the engineer and painter must give particular heed. Several factors contribute to this, but the most important are as follows :—

1. We have already seen that both air and liquid water are essential to corrosion. At its surface, in contact with the ordinary atmosphere, water is practically saturated with oxygen, and its corrosive powers are consequently at a maximum. Furthermore, as fast as the water gives up its oxygen to any iron object, just so fast can it absorb more from the air, for, being at the surface, it has not to wait for the oxygen to diffuse leisurely through several superincumbent layers of water, as is the case for a point some distance below the surface. The rate of corrosion is thereby greatly enhanced.

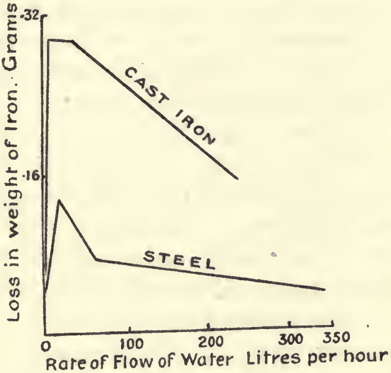

FIGURE 22.—CURVE SHOWING EFFECT OF RATE OF FLOW OF WATER UPON THE CORROSION OF CAST IRON AND STEEL.

2. It never happens that the surface of water is absolutely still in nature, and tiny waves alternately wash the surface of the

iron for a small space, and then leave it to dry. The thin film of water thus tends to partially evaporate before it is renewed by a second wave, and the concentration of any salts which it may contain dissolved in it increases for the time being, thereby accelerating the rate of corrosion. When a second wave comes along the process begins over again. As this goes on indefinitely, a marked difference will be caused in the corrosive action in the course of time, due to this cause alone.

3. As we shall see in a later section, light is a powerful stimulator of corrosion, and those parts of iron columns, etc., near to the surface of water in exposed places are considerably more brightly illumined than are those further down, owing to the absorption of light by the water; consequently corrosion proceeds with greater vigour at the surface.

4. Warm water being lighter than cold always rises to the top, so that reactions which are favoured by a slight rise of temperature may be expected to take place with greater rapidity near the surface of the water. In warm weather, therefore, the superficial layers of water will become appreciably warmer than those a little lower down, and heat will travel but slowly downwards owing to the poor conductivity of the water. Consequently the rate of corrosion of iron near to the surface is accelerated. As we shall see in a later section, an alteration in the temperature introduces a host of new factors, so that its direct influence upon the rate of corrosion is a very uncertain quantity, its magnitude depending to a large extent upon local conditions obtaining at the time.

In actual practice the observed effects are due to a combination of these factors, their relative influence and importance being determined by local conditions.

THE PHYSICAL CONDITION OF THE IRON.

The physical condition of the iron is a matter of no small importance where its liability to corrode is concerned. We have already seen in an earlier chapter[1] that pulverized iron can be observed to effect the decomposition of steam at considerably lower temperatures than iron in the compact form; and the principle may be expected to apply in the ordinary process of rusting. Practice shows that a brightly polished, smooth surface, such as that presented by a razor, is far less likely to rust than is a rough-filed or porous mass, for here capillary forces and surface tension play a part, the magnitude of which it is difficult to determine. Porous bodies are particularly susceptible to corrosion, because moisture condenses within the pores and is very slow to evaporate. Consequently rusting proceeds apace even in a fairly dry atmosphere in which a polished surface would remain untarnished. Herein, no doubt, is to be found a partial explanation for the relatively greater corrodibility of the coarser grades of cast iron over that of the finer sorts, although this is not the only explanation. Clement[1] illustrated many years ago in a singularly graphic and beautiful manner the remarkably porous nature of the coarser grades of cast iron. A turned and bored cylinder of the metal was placed within a copper cylinder and the intervening space filled with molten tin. On cooling, some of the tin was found to have been squeezed through the cast iron, and appeared as a fine filamentous wool lining its interior. It was so tenuous as to burn readily in a candle flame.

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[1] See Chapter III.

Jouve[2] has recently called attention to the increase in weight observed after cast iron vessels containing a high percentage of silicon have been used for the evaporation of acids, particularly sulphuric acid. This he attributes to the porosity of the metal. Clearly the closer the grain of the cast iron, the better fitted it is to resist corrosive influences, and this fact is acknowledged in practice. Reference may here be made to Juncker's[3] very ingenious suggestion that the corrosion of cast iron might be reduced by forcing linseed oil under pressure into its pores, and allowing it to set or dry.

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[1] Clement, "Quarterly Journal," **2**, 385; quoted by Mallet, "British Association Reports," 1838, 267.

[2] Jouve, "J. Iron Steel Inst." 1908, III, 310.

[3] Juncker, quoted by Mallet, "British Association Reports," 1838, p. 276.

M. Thornton Murray[1] has drawn attention to the fact that steel cables offer considerable opportunity for rusting, because the interstices between the strands or wires of the cable behave virtually, as pores, and, by effecting the condensation of water, greatly accelerate the speed of corrosion. Cables have in consequence been found which present to the outward eye the appearance of great solidity and strength, but on examination have exhibited such intense internal corrosion as to render them unfit to bear the slightest strain.

Any condition of twist or strain is liable to set up serious corrosion in the parts affected, even though the chemical compositions of the strained and unstrained portions are identical. The cause, therefore, is entirely due to physical differences which set up a potential difference between the strained and normal parts, resulting in local corrosion.[2]

THE ACTION OF LIGHT.

Apparently the first to make an attempt at quantitatively determining the effect of light upon the rate of corrosion of iron were Cribb and Arnaud.[3] The results obtained by these investigators are given in brief in the accompanying table :—

THE EFFECT OF LIGHT UPON THE RATE OF CORROSION OF IRON.

Liquid in which the Iron was Immersed.	Duration of Experiment. Hours.	Loss in Weight of Iron Expressed as m.grm. of Fe_2O_3. (In Dark.)	(In Light.)
Distilled water . . .	12	4·5	6·5
,, . . .	240	9·5	39·5
Tap water	24	7·5	13·5
River water	240	21·7	56·0
Distilled water containing in 100,000 parts :—			
$MgCl_2$, 20 parts . .	24	5·2	7·2
$NaHCO_3$, 84 ,, . .	24	6·0	8·5
Na_2CO_3, 53 ,, . .	24	5·0	7·0
$Ca(OH)_2$, 9·2 ,, . .	24	7·2	11·5
NaOH, 4 ,, . .	12	2·0	4·2

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[1] Murray, " J. Iron Steel Inst." 1910, I, 703; from a paper read before the Chemical, Metallurgical, and Mining Society of S. Africa.

[2] This branch of our subject is dealt with in full detail in Chapter XIV.

[3] Cribb and Arnaud, "Analyst," 1905, **30**, 225.

These results speak for themselves, showing very clearly that the rate of corrosion of iron is greatly increased by exposure to the action of diffused sunlight. It is unfortunate, however, that details are not given in the original memoir as to the superficial area of the iron plates used, etc. as these would have been most valuable.

Friend has studied the subject in somewhat greater detail. Pieces of pure iron foil, measuring 4 × 5 cm. in area, were placed in a series of beakers, one piece of foil in each beaker, and covered with 100 c.c. of tap water. The four corners of the plates rested in contact with the sides and bottom of the containing vessels. One series was placed in a dark cupboard whilst the other stood in front of a large window in the same laboratory, exposed to the action of the diffused sunlight. Irregular illumination was prevented by large sheets of Muranese glass, which broke up any direct light. At varying intervals of time a piece of iron was taken from each series, cleaned and weighed, the loss in weight being regarded as a direct measure of the corrosion. The results obtained are given graphically in Fig. 23. The irregular nature of Curve II. is undoubtedly attributable to variations in the intensity of the sunlight during the time of exposure. The real effect of the light would of course be much greater than that indicated by these results, for, during the night-time its stimulating action was withdrawn, the two sets of plates being then under similar conditions.

From these considerations it is obvious that corrosion will proceed less rapidly in boilers, covered tanks, dark cellars, and the like than would otherwise be the case under precisely similar conditions if light could gain access.

In a previous section we have already dealt with the corrosion of iron plates immersed in water at various depths below the surface, and have drawn attention to the fact that, the greater the depth, the slower is the rate of corrosion. The experiments of Heyn and Bauer were quoted as giving a practical demonstration of this fact. These experiments, however, were carried out in glass vessels uniformly exposed to the action of diffused sunlight, so that the lower plates received the same amount of illumination as the upper ones. In actual practice, however, such is rarely the case, for it usually happens that the lower parts of bridge columns, ships, etc., are much less brilliantly illuminated than those parts lying near the surface of the water, so that in these cases a still more pronounced difference in the relative rates of corrosion is observable, other things of course being equal.

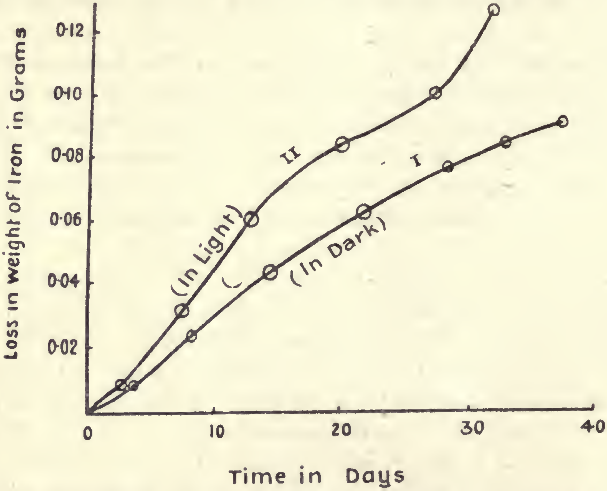

FIGURE 23.—CURVE SHOWING THE ACCELERATING INFLUENCE OF LIGHT UPON THE CORROSION OF IRON.

In order to practically demonstrate this, Friend immersed two plates of pure iron foil, measuring 7·5 × 4·4 cm. in area, in a tall glass cylinder, one plate being 9 cm. below the surface of the water, and the other 70 cm. The plates were suspended vertically by means of glass hooks, interference through galvanic action thus being avoided. The whole was placed near to a large window, covered with Muranesė glass, and thus exposed to an illumination which was very uniform throughout its length.

Two more plates of exactly the same size were immersed to the same depth in a precisely similar manner in another cylinder, save that the latter was surrounded throughout its length by a sheet of stout brown paper, being thus open to the light at the surface of the water, and but imperfectly illuminated below, although not absolutely dark—a condition of affairs closely approximating to those obtaining in a deep pond. After the lapse of nine days the plates were withdrawn, cleaned, and weighed in the usual manner. The results are given in the following table:—

THE COMBINED EFFECT OF DEPTH AND DARKNESS UPON THE RATE OF CORROSION.

Depth of Immersion. Cm.	Loss in Weight When Both Plates Illuminated. Grm.	Difference. Grm.	Loss in Weight When Top Only Illuminated. Grm.	Difference. Grm.
9	0·0983	0·0151	0·1003	0·0305
70	0·0832		0·0698	

These results show very clearly the stimulating activity of proximity to the surface and of free access of diffused sunlight. It is noteworthy that the difference between the amounts of the two illuminated plates is almost exactly doubled when the lower one is darkened, showing that the retarding action of depth is equal to that induced by darkness. This is, of course, purely fortuitous in this case, but serves to show what an important factor even diffused sunlight may be in cases of corrosion.

RISE OF TEMPERATURE.

It is well known that an increase in the temperature of two or more reacting substances has a marked stimulating effect upon their chemical activities. In the case of the corrosion of iron the whole problem is greatly complicated by the fact that a rise of temperature immediately introduces a host of new factors of varying importance. In all ordinary cases of corrosion, therefore, the influence of temperature is very uncertain, its magnitude depending very largely upon the local conditions obtaining at the time.

In order to simplify matters let us first of all consider the case of pure iron immersed in distilled water. On raising the temperature we have two opposing forces to consider:—

1. With rise of temperature the combined affinity of oxygen and water for iron rapidly increases, as is usual in such cases, and this tends to accelerate the rate of corrosion.

2. Opposed to this, however, we have the decreased solubility of oxygen and of gases generally in water as the temperature rises, until at the boiling-point the solubility coefficient is nil, and iron may be kept in contact with such water for an indefinite time, without undergoing any apparent change.

The actual amount of corrosion which takes place at any time will thus depend upon the resultant of these two forces, and there must be some temperature at which this corrosion is a maximum.

Mallet[1] states that in shallow waters the maximum amount of oxidation took place at from 79° to 88° C., for oxygen was then able to diffuse towards the iron and to rapidly unite with it. If the water be agitated or made to flow over the iron, the amount of corrosion will be greatly increased, and the temperature of maximum corrosion will undergo considerable variation according to circumstances.

Heyn and Bauer[2] have very recently studied the subject in detail. Pieces of steel,[3] measuring 4·5 × 3 cm. in area, were suspended by glass hooks in a tube containing water and fitted with a vertical condenser, as shown in Fig. 24. The tube was maintained at certain definite temperatures for a period of twenty-two days by immersion in a glycerine-bath, whose temperature was kept constant by means of a thermo-regulator. The results obtained are shown graphically in Fig. 25.

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[1] Mallet, "British Association Reports," 1840, p. 229.

[2] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1910, **28**, 104.

[3] For analysis of the steel, see p. 129.

It will be observed that the corrosive action reaches a maximum 60° C. or thereabouts. A separate series of experiments was carried out by Heyn and Bauer, in which the pieces of metal were heated to a given temperature for a period of seven hours only each day, for twenty-two days. During the intervening time they were allowed to cool down to the temperature of the room. In this case the maximum corrosion took place at approximately 80° C., a result in close accordance with that given by Mallet, to which reference has already been made.

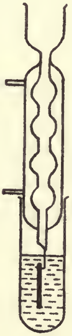

Figure 24.—Heyn and Bauer's Apparatus for Determining the Corrosion of Iron at Various Temperatures.

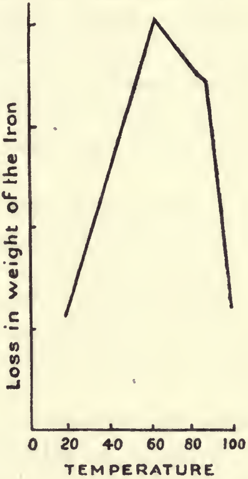

Figure 25.—Showing the Relative Rates of Corrosion of Iron Immersed in Water at Various Temperatures.

In actual practice, however, the condition of affairs is rarely so simple as this, the whole problem being complicated by the introduction of new factors of variable importance, the chief of which are as follows :—

1. Unequal heating. A large mass of metal, such as the shell of a ship, cannot well be subjected to a uniform rise of temperature throughout its entirety. Consequently electrical activity is set up between the cool and the warm portions resulting in increased corrosion.

2. The non-metallic impurities of ordinary commercial iron, such as, for example, sulphur and phosphorus, are liable to oxidize as the temperature rises, yielding acids which enormously accelerate corrosion.

3. The water used in boilers frequently contains small quantities of soluble salts which tend to hasten any corrosive action.

4. Electrical or galvanic activity, due to irregular composition of the metal, to segregation, to contact with other similar and dissimilar metals, and so on, and which may be capable of slowly exerting an influence upon the corrosion of the iron at ordinary temperatures, becomes greatly enhanced as the temperature rises, so much so as to yield quite astonishing results.

Other minor factors will no doubt occur to the reader, but each of the above will be fully discussed, as occasion requires in the sequel.

The Presence of Rust.

When iron has once begun to rust in air, further corrosion proceeds rapidly, until the whole surface of the metal is oxidized, even although the temperature of the air is well above dew-point, so that a piece of bright iron exposed in a similar manner would remain unaffected for an indefinite time. In this respect the rust seems to play an analogous part to disease in the animal or vegetable organism. In reality, however, there is not the slightest connexion between the two classes of phenomena.

Two theories have been advanced to account for this corrosivity:—

1. Kuhlmann[1] suggested that the rust acted as an oxygen carrier, and thus catalytically assisted further corrosion.

2. A second theory suggests that the action is due to the porosity of iron rust. Bauermann[2] stated some years ago that a unit of malleable iron produces ten volumes of rust. Now since the rust is very hygroscopic it soon becomes charged with liquid water, which fills its pores, and is very slow to evaporate. This, therefore, stimulates corrosion in a moist atmosphere in which bright iron would not be effected. This view was held by Hutton,[3] Crace Calvert, Wagner, Crum Brown, and others, and has been received with increasing favour down to the present time.

Previous to 1908 neither of these theories had received satisfactory experimental verification. Friend[4] therefore carried out a few experiments in order to settle the point, and his results showed conclusively that the latter theory is correct.

(*a*) Several tubes were hermetically sealed, each containing air, 1/30 normal sodium hydroxide solution[5] and a piece of pure iron foil, half of whose surface had been allowed to rust, whilst the remaining half was polished. After several months it was found that not only had the rusted portion not increased in area, but some of the rust had been loosened and lay at the bottom of the tube.

(*b*) The above experiments were repeated using a dilute solution of chromic acid instead of sodium hydroxide. The results were identical. This is all the more remarkable since chromic acid is such a powerful oxidizer, and had the rust possessed the power to act as an oxygen carrier, as Kuhlmann suggested, these conditions would have been exceptionally favourable to the reaction.

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[1] Kuhlmann, see Dammer, "Handbuch der anorganischen Chemie," 1893, III, 303.

[2] Bauermann, "J. Iron Steel Inst." 1888, II, 135.

[3] Hutton, "Chem. Zentralblatt," 1872, p. 819; Crace Calvert, "Dingler's Polytechn. J." 1870, **196**, 129; Wagner, *ibid.* 1875, **218**, 70; 1860, **157**, 153; Crum Brown, "J. Iron Steel Inst." 1888, II, 129.

[4] Friend, "J. Iron Steel Inst." 1908, II, 22.

[5] Such a solution contains 1·33 grm. of NaOH per litre.

(*c*) A part of the cylinder AE (Fig. 11, p. 61), used in the investigation previously referred to, was allowed to rust in air. It was then introduced into the flask, washed with potash, and subjected to continuous washing with condensed water vapour in the manner already described.

The patch of rust did not increase in area however.

All these experiments definitely prove that rust does not act as an oxygen carrier, but that its corrosive influence is to be attributed to its porous nature.

The corrosive action of rust is somewhat different when the metal is totally immersed in water, for here the porosity of the oxide has little to do with it. The reaction is undoubtedly due to galvanic action consequent upon a difference of potential between the rust and unaltered metal, leading to rapid, localized corrosion. We shall deal with this aspect of the question very fully in Chapter XIV.

In this connexion it is interesting to observe that "busy" iron rusts far less rapidly than idle metal exposed to the same corrosive influences. This is a matter of universal observation and acknowledgment amongst practical men. J. M. Heppel[1] states that some disused rails lying in a yard at Madras in India, exposed to the sea air, had lost about 1 lb. in weight per foot, whereas similar rails in service hard by were not perceptibly affected. Commenting upon this, Sang writes: "The top of a rail is compressed and smoothed down in service by the grinding of wheel tires, for there is always a certain amount of slip, especially during acceleration and retardation. Galvanic action between the smooth head of the rail and the rest of it has been suggested to explain this immunity from rust, but it is not at all likely that the foot would owe its protection to the thin stratum of denser metal so far removed from it. If that dense skin on the top of the rail were not crushed beyond its elastic limit, it would, on the contrary, tend to accelerate the corrosion of the steel in contact with it. The real reason for this difference of behaviour seems to lie in the observed fact that oxidation is apparently arrested, or at least greatly retarded, by vibration. Explanation seems to stop at this point, but a simple theory can be built on the assumption that the vibration causes a shedding of the rust, as soon as it is formed on the spots that are not protected by mill scale, and there is, therefore, no acceleration of the action due to the accumulation of spongy and electronegative rust."

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[1] Heppel, quoted by Sang, "Proc. Eng. Soc. West. Pa." **24** (10) 523. See "Corrosion and Preservation of Iron and Steel," by Cushman and Gardner, 1910, p. 108.

No doubt this is a partial explanation, but, as we have already seen,[1] the freedom from rapid rusting may be due in part to the rise in temperature caused by the rush of the trains over the metals, whereby the rails are maintained at temperatures slightly above that of their surroundings. The result is that liquid water has no good opportunities of condensing upon them, or, if once condensed, it is rapidly vaporized and corrosion retarded.

Countless analyses of rust have been made and published, and serve to illustrate how variable is its composition, depending as it does upon local circumstances. They do not, however, in general throw much light upon the mechanism of corrosion, and we shall not consider them in detail.[2]

THE EFFECT OF TIME.

The effect of prolonged exposure to corrosive influences is a very variable and but ill-understood quantity. A glance at the curves shown in Fig. 23 (p. 92) will suffice to impress the reader with the fact that, except for very short intervals of time, the extent of corrosion exhibited by pure iron plates immersed in water is not proportional to the length of exposure to the same. In other words, the expression

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[1] See p. 19.

[2] The following references may prove useful to the reader desirous of becoming acquainted with these analyses: Gaines, "Chemical News," 1910, **101**, 205. Tilden, "Trans. Chem. Soc." 1908, **93**, 1358; Moody, *ibid.* 1906, **89**, 720; Dunstan, *ibid.* 1905, **87**, 1548; Jamieson, "Min. Proc. Inst. Civil Engineers," 1881, **65**, 323; Calvert, "Chem. News," 1871, **23**, 98.

$$T \propto C$$

where T and C stand for time and corrosion respectively is only approximately true, even when two periods of time are being considered which do not differ greatly from one another.

It may be argued, however, and with reason, that these curves were obtained not by measuring the rate of corrosion of any one piece of metal for varying periods of time, but by using a series of plates, and assuming that they were all corroding at the same rate.

Now the only method by which the rate of corrosion of a single metallic plate could be followed without disturbing the system during the course of the experiment would be to measure the volume of oxygen absorbed. This has been done by Friend, who immersed a plate of wrought iron, measuring 7·65 × 2·9 cm. in area and weighing 16·5 grm. in 100 c.c. of tap water, containing a little common salt to assist the corrosion. The bottle containing the metal and solution was maintained at 20° C. in a thermostat, and connected externally to an oxygen supply so arranged that the volume of gas absorbed could readily be determined at any time. The results obtained are shown graphically in Fig. 26. It will be observed, however, that the curve has the same general form as those in Fig. 23, and thus confirms those results. Owing to the fact that some ferrous oxide is almost always formed during the corrosion of iron immersed in water, which means that more iron is in reality attacked per unit of oxygen absorbed than would otherwise be the case, the results obtained by weighing several iron plates, as previously done, are undoubtedly more accurate.

From the curves obtained by either method, however, the following facts may be gleaned :—

1. Corrosion at first proceeds with much greater rapidity than is afterwards the case.

2. As the time of exposure is greatly prolonged, the rate of corrosion gradually decreases and becomes more nearly proportional to the time.

This, however, is only true when the metal used is fairly pure, and the conditions of the experiment are unvaried. In actual practice, on the other hand, the conditions are rarely uniform, even if the metal itself is fairly pure, so that the whole problem is greatly complicated.[1]

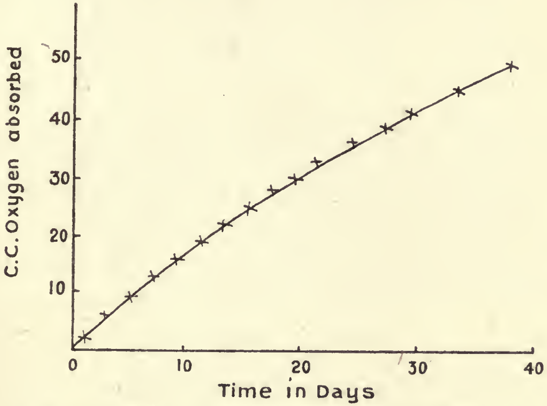

FIGURE 26.—CURVE SHOWING THE ABSORPTION OF OXYGEN BY A PIECE OF IRON DURING RUSTING.

K. Arndt[2] has recently measured in a similar manner the amount of oxygen absorbed during the corrosion of iron and steel, and his results are worthy of consideration at this point.

Iron tubes, 20 cm. long and 6 cm. in diameter were placed on paraffin blocks over water in glass cylinders, and the volumes of oxygen absorbed determined by a Hempel burette. The results obtained are given in the following table :—

[1] See Schuhmann, "Iron Age," 1908, **81**, 520.

[2] Arndt, "Chemiker Zeitung," 1910, **34**, 425.

THE RATE OF ABSORPTION OF OXYGEN BY IRON AND STEEL.

Time in Days.	c.c. of Oxygen absorbed by:—		
	Cast Iron.	Mild Steel.	Weldless Tube.
1	13	13	5
3	24	32	8
5	30	45	30
10	45	63	109
20	59	108	198
30	73	156	293
43	95	213	389

It is noteworthy that, although at first the cast-iron corrodes quite as rapidly as the steel, as the time progresses its rate of corrosion becomes reduced out of all proportion to the others. This is quite in accordance with experience, for cast iron articles have been repeatedly proved to offer a very high resistance to the corroding influences of time.

BIOLOGICAL INFLUENCES.

When iron structures are allowed to corrode in a natural manner, by exposure to atmospheric influences and to the action of the soil generally, teeming, as it is, with animal and vegetable life, many curious complications often arise.

Richard Gaines[1] has recently emphasized the need for reckoning with bacterial activity as a corrosive influence in the soil. Upon analysing a number of rust tubercles and pits taken from steel conduits situated in different parts of the country (America), it was observed that abnormal amounts of sulphur were present. For example, six analyses of rust from different conduits yielded the following percentages of sulphur (calculated as SO_3):—

1. 1·41, 2·25, 2·98, from "tubercles" on the interior of three pipes,

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[1] Gaines, "Chemical News," 1910, **101**, 205.

2. 1·51, 3·95, 6·50, from "pits" on the exterior of other three pipes.

This abnormal amount of sulphur could not be attributed to a high sulphur content in the steels, for analysis showed that the unattacked interior portions of the metal of the conduits contained only 0·05 per cent and less, of this element, and as the percentage of manganese in the rust was no greater than that in the steel, abnormal segregation and consequent corrosion of the manganese sulphide was likewise rendered an untenable supposition. Gaines therefore suggests that certain sulphur bacteria are the underlying cause of this phenomenon, and, although no definite proof of the assumption is brought forward, very plausible arguments are advanced in its favour. Gaines also mentions a serious case of corrosion which had been brought before his notice. During the execution of certain repairs in connexion with the foundation structure of a bridge across Lake Hauser in Montana, the attention of the chief engineer was directed to numerous protuberances which occurred with moderate regularity upon the steel work. The workmen called this corrosion "shell rust," and stated that it was often to be seen on steel which had been under water for some time. Specimens of the rust were submitted to Schorler, who identified *Gallionella ferruginea* in great abundance in the material. This organism apparently attacks the iron by excreting some acid material in which the metal dissolves. The structural damage is stated to have been enormous for the short period of one year during which the bridge had been in service. These observations confirm those of earlier writers[1] and serve to show very clearly how far-reaching the action of these minute organisms may be in respect of the corrosion of iron.

Turning our attention now to larger forms of animal life, the worms must be considered as being possibly very destructive agents where iron embedded in the soil is concerned. We do not generally realize what an enormous amount of work is done annually by our land worms, although no reader of Darwin's famous "Vegetable Mould and Earthworms" can be insensible to its importance. Hensen calculates that 53,767 worms exist in an acre of land, but this is based upon the number found in gardens, whereas he believes that only half as many live in cornfields, and since gardens occupy a relatively small portion of the land, we may assume for the purposes of calculation that this lower number, namely 26,886 worms, is more nearly correct. Darwin estimates that each worm annually ejects 20 ounces of soil as castings; that is to say, no fewer than 15 tons of soil pass through the bodies of worms every year in each acre of land. Now the interesting feature of this is that worm castings are generally acid when fresh. Darwin mentions that thirty castings from different places were tested, and with but three or four exceptions all proved to be acid. The neutrality of the exceptions is attributed to their not having been fresh at the time of testing; for some which were at first acid were, on the following morning after having been dried and again moistened, no longer acid. Darwin further states that H. Johnson found 0·018 per cent of ammonia in certain worm castings. Remembering, then, that 15 tons of soil per acre are, on the average, rendered acid by worms and charged with small quantities of ammonium salts every year, it is easy to see that a stimulus of some sort must be afforded in this way to iron work planted in the soil. That the acids present in the bodies of worms are very powerful may be inferred from an interesting series of experiments carried out by Darwin. Some worms were kept in a pot filled with fine red sand, the red colour being due to ferric oxide. The burrows which the worms made through this sand were lined as usual with their castings, formed of the sand mingled with their intestinal secretions and the refuse of the digested leaves. Now this sand was observed to have entirely lost its red colour, examination under the microscope showing that the ferric oxide had been completely dissolved out. Acetic acid hardly produced any effect upon this sand, and even the stronger mineral acids, hydrochloric, nitric, and sulphuric, when diluted as in the pharmacopœia, produced less effect than did the acids in the intestines of the worms.

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[1] Schorler, "Centralblatt Bakter- und Parasiten-kultur," 1904, **12** (ii.) 681; 1905, **15**, (ii.), 564. Beythien, "Zeit. Unters. Nahr- Genussm." 1905, **9**, 529. Adler, "Centralblatt Bakter- und Parasiten-kultur," 1904, **11** (ii.), 215. Raumer, "Zeit. anal. Chem." 1903, **42**, 590.

Remarkable as it may seem, therefore, the insignificant worm must be reckoned with as a factor in the corrosive influences at work upon our iron structures.

Nor is the animal world the only branch of those living organisms which aid in the destruction of iron work, for plants are likewise capable of doing an enormous amount of work. Young roots, and especially root hairs, in addition to exhaling carbonic acid, excrete stronger acids or acid salts by means of which they dissolve insoluble bodies. That this is the case is readily demonstrated by allowing the roots to grow upon a polished plate of marble, when the latter will be so corroded as to exhibit an etched pattern showing the path of the roots. By placing the roots upon paper dyed with litmus or other sensitive indicator their acidity may readily be demonstrated. Furthermore, when plants decay, humus acids result which are powerful solvents. We thus see that in numerous ways plants may contribute in no small degree to the corrosion of iron work in the soil.

It is unnecessary to carry these thoughts further, for the reader will by now have easily grasped the underlying principle, and perceive that the question of the corrosion of iron embedded in the soil may, after all, not be so simple as would appear at first sight.

SUMMARY.

Sufficient has now been said to show how complicated the whole subject of corrosion is even in its simplest cases. In practical life, however, the problems are rendered tenfold more difficult by the fact that we are dealing in the main, not with relatively pure iron, air, and water, but with these substances contaminated with all kinds of impurities. Local galvanic action frequently arises between two pieces of metal at their points of contact, causing serious corrosion; and a similar action occurs at points on or near the surface of iron sheets, resulting in pitting and destruction, due to the action of traces of cinder, oxide, or other foreign material. Natural waters are not infrequently contaminated with sewage, and numerous other corrosive ingredients used for domestic purposes or bye-products of some factory. The air of our towns and cities is rendered acid by the presence of sulphur and nitrogen compounds eliminated during the burning of coal or the commercial manufacture of some necessary commodity. What wonder then that the story of corrosion has, in the past, been only too often one of confusion and error. It is only recently that we have begun to realize its magnitude and to attack the problems along scientific lines. There can be no doubt that during the next few years rapid advances will be made in this direction, and that the numerous questions which baffle us to-day will then receive satisfactory solution.

In the succeeding chapters we shall consider as fully as possible the influences of the numerous special factors alluded to above as affecting the corrosion of iron structures in practical life.

VII.

THE ACTION OF ACIDS UPON IRON.

WHEN aqueous solutions of the majority of acids act upon iron, the metal passes into solution with the formation of a ferrous salt, an equivalent amount of hydrogen gas being simultaneously evolved. Thus, for example, if hydrogen chloride is the acid employed, ferrous chloride and free hydrogen are the ultimate products. This change may be represented by the following equation :—

$$Fe + 2HCl = FeCl_2 + H_2$$

provided air or oxygen be absent. Should these gases be present, however, and an excess of acid not be employed, the iron is rapidly oxidized to the ferric condition. Whether or not in this case a precipitate forms will depend upon the conditions of the experiment. Even if a large excess of acid be present, oxidation will still proceed, but much more slowly. If only a trace of acid be there, the iron will be thrown out of solution as hydrated ferric oxide or rust, as we have already seen.[1] If sufficient acid be present to combine with all the iron, a soluble ferric salt may result. Thus, for example, referring again to the action of hydrogen chloride upon iron, some such reaction as the following would take place :—

$$4FeCl_2 + O_2 + 4HCl = 4FeCl_3 + 2H_2O$$

The completeness of oxidation must obviously be dependent upon a plentiful supply of air or oxygen. Should, on the other hand, an iron salt be formed which is insoluble in the liquid, this will tend to form a layer of varying thickness over the surface of the metal, and preserve the underlying portion from attack. In this case only a relatively small percentage of the metal will be acted upon, depending upon the extent of the exposed area. Such is the case with strong sulphuric acid at ordinary temperatures, provided but little water is present.[1]

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[1] See Chapter IV.

An interesting complication occurs in the case of those acids that possess a considerable quantity of loosely attached oxygen and thus are, at the same time, both acids and oxidizers. Nitric and chromic acids are cases in point. When they act upon iron, hydrogen gas is not in general evolved, that element being oxidized to water at the expense of the oxygen content of part of the acid. We may assume that, as the iron dissolves, it yields primarily a ferrous salt and that this is rapidly converted to the ferric condition by the excess of acid, even in the entire absence of air. It has been observed, however, that when certain concentrations of these acids are employed the iron is very little acted upon and, although its surface not infrequently remains perfectly bright and apparently unaltered, the metal is found to be inactive towards certain salt solutions, such as those of the sulphates of silver and copper, in which in ordinary circumstances it dissolves with ease. The iron is therefore said to have been rendered passive, and a full discussion of this condition is reserved for a later chapter.[2]

Attention has frequently been called by different, independent investigators to the fact that, when a piece of iron has been exposed for a short time to acid attack, the undissolved residue exhibits a very marked change in its physical properties, and only returns to its original condition after a considerable lapse of time. W. H. Johnson[3] appears to have been the first to study this phenomenon and to bring the matter before the Literary and Philosophical Society of Manchester during the session 1873-4. His experiments were subsequently detailed in the Proceedings of the Royal Society of London. In 1880 Hughes rediscovered the phenomenon and is generally regarded as the original discoverer, although, as we have already seen, he had been anticipated by Johnson by fully six years.

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[1] See Lunge, "Chemisches Repertorium," **10**, 86; A. Larsson, "Teknisk Tidskrift," 1893, p. 32.

[2] See Chapter XII.

[3] W. H. Johnson, "Proc. Roy. Soc." 1875, No. 158.

After immersion in very dilute sulphuric acid, pieces of soft charcoal iron wire were observed by Johnson to become quite brittle, and on moistening with water frothed up as though acted upon by a powerful acid. The metal returned to its original condition again, however, after the lapse of a few days at the ordinary temperature, and in the course of a few hours, if gently warmed.

Struck by this remarkable behaviour of the iron, Osborne Reynolds[1] still further investigated the matter. Obtaining a piece of wrought iron gas pipe, 6 inches long, 0·6 inch in external diameter, and 0·0625 inch thick, he cleaned it thoroughly and sealed one end by soldering on a copper disc. The open end was attached to a glass tube by a piece of india-rubber and completely filled with oil (Fig. 27). On immersing the iron tube in dilute sulphuric acid, gas, which subsequently proved to be hydrogen, collected in the glass tube. The action was particularly rapid if the whole was warmed. Clearly the hydrogen gas formed by the action of the acid upon the external surface of the iron tube had passed through the metal.[2] The apparatus was now disconnected and the iron tube cleaned with cold water and soap to remove all acid and oil, after which treatment it was immersed in hot water. A vigorous frothing en-

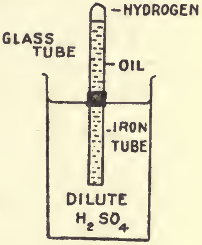

FIGURE 27.—APPARATUS USED BY REYNOLDS TO SHOW THAT IRON IS POROUS TO HYDROGEN GAS.

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[1] Osborne Reynolds, paper read before the "Manchester Literary and Philosophical Society," 24 February, 1874.

[2] That hydrogen could pass through an iron vessel immersed in sulphuric acid had already been shown by Cailletet, "Compt. rend." 1863, 66, 847.

sued showing a liberation of hydrogen; but by and by the effect passed off. By these experiments Reynolds satisfied himself that the curious phenomena described by Johnson were due entirely to occluded hydrogen. This conclusion was independently confirmed by Hughes in 1880, who found that iron wires, treated with sulphuric acid, as indicated above, contained twenty times their volume of hydrogen in addition to those three to ten volumes of other gases normally present in the metal.

Some thirteen years later Ledebur[1] again directed attention to these phenomena, making a careful quantitative study of the same. This investigator made use of various kinds of iron and steel wire obtained from two firms in the Erzgebirge, and which were intended for the manufacture of wire ropes. The wires varied in diameter from 0·065 to 0·140 inch and were immersed for varying periods of time in acid under the following conditions:—

Series I.—The wires were not cleaned, but immersed direct in 1 per cent sulphuric acid (by weight) for twenty-four hours, and examined three days later.

Series II.—Grease was removed from the wire with ether, after which the metal was immersed for a period of twenty-three hours in dilute sulphuric acid, containing one part of acid and forty parts of water. The wire was then withdrawn and examined immediately.

Series III.—Each wire was dipped in acid of similar concentration to the last-named, but was connected with a block of zinc to set up galvanic action. After three hours, during which time hydrogen gas had been rapidly evolved, the wires were removed and tested.

Series IV.—Precisely similar to Series III but the wires were not tested until four days after their removal from the acid.

Series V.—Precisely similar to Series IV, save that the wire after immersion in the acid was heated to cherry red in an inert atmosphere for fifteen minutes.

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[1] Ledebur, "Stahl und Eisen," 1887, 7, 681.

The results of these experiments are given in the following table:—

LEDEBUR'S RESULTS.

Number of Series.	Tensile Strength in Tons per Sq. Inch.		Elongation on 3·94 Inches. Per cent.		Number of Times the Metal could be Bent.	
	Before.	After.	Before.	After.	Before.	After.
I	54·54	54·66	3·5	2·8	10·2	8·0
II	54·09	56·00	3·4	2·7	7·4	3·0
III	52·76	52·19	2·0	2·2	10·0	3·9
IV	51·11	51·17	3·0	2·2	10·1	7·2
V	27·24	28·51	17·9	16·9	16·2	14·6

From these experiments we see that:—

1. When hydrogen is evolved upon the surface of metallic iron the physical character of the metal is altered, whilst the tensile strength remains substantially the same, the elongation lessens and the brittleness increases.

2. Contact with zinc whilst immersed in the acid causes this action to be still more pronounced.

3. Exposure to air at the ordinary temperature gradually causes the iron to assume its original condition. Annealing at cherry red heat rapidly removes the brittleness.

Further experiments showed that cast iron is, on the whole, less affected by immersion in acid than is malleable iron. The latter is rendered brittle in a few hours even by very dilute acid, whereas cast iron was found to require nine days' exposure to relatively strong acid to produce a well-defined effect. This is attributed by Ledebur to the greater percentage of silicon which the latter metal contains.

Let us now pass on to consider the action of the commoner acids upon iron individually.

CARBONIC ACID.

When carbonic acid acts upon iron in the absence of air, its behaviour is comparable with that of hydrochloric acid, a regular stream of hydrogen gas being evolved, and ferrous carbonate passing into solution as the acid salt, $FeH_2(CO_3)_2$. Thus :—

$$Fe + 2H_2O + 2CO_2 = FeH_2(CO_3)_2 + H_2.$$

If the supply of carbonic acid be limited and excess of iron be present, the whole of the hydrogen is replaced by iron, the insoluble normal carbonate resulting. Thus :—[1]

$$Fe + H_2CO_3 = FeCO_3 + H_2.$$

Carbonic acid is generally regarded as being of such a weak nature as to be incapable of acting upon iron to any very great extent within reasonably short periods of time. Moody,[2] however, shows that the action is, on the contrary, very appreciable. Five hundred grm. of clean iron borings were immersed in 250 c.c. of a saturated solution of carbon dioxide in water at atmospheric pressure, the amount of iron passing into solution being determined at intervals. The results obtained were as follows :—

	Grm. of FeO per Litre.
After 20 hours	0·2546
{30 {56 „	0·3771
96 „	0·8172
26 days	2·139

In the absence of air the solution remained practically colourless, but was readily decomposed on admission of oxygen yielding a complex mixture of ferrous carbonate, ferrous hydroxide and ferric hydroxide in varying proportions.

The rate at which this last-named reaction takes place has been recently made the subject of careful study by Just,[3] but it is beyond the scope of this work to enter into a full discussion of the results obtained. It is shown that the greater the amount of oxygen admitted, the more rapid is the decomposition of the carbonate. On the other hand, excess of carbon dioxide tends to hinder the reaction, whereas the presence of ferric hydroxide has no effect whatever.

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[1] Bruno, "Bull. Soc. Chim." 1907 (iv.), **1**, 661.

[2] Moody, "Trans. Chem. Soc." 1907, **89**, 727.

[3] Just, "Zeit. physikal. Chem." 1908, **63**, 385.

This is precisely what we might expect from theoretical considerations, and the importance of these results will be obvious. Owing to the ease with which ferrous carbonate decomposes in the presence of air, it is easy to see that a definite weight of carbonic acid will exert a greater corrosive action upon iron than will an equivalent quantity of a stronger acid, such as hydrochloric or sulphuric, other things being equal.

SULPHURIC ACID.

More attention has been given to the action of dilute sulphuric acid upon iron and steel than has been devoted to a study of all other acids put together, with the exception, possibly, of nitric acid, and this for a variety of reasons. Being commercially cheap and easily procured, its only serious rivals are hydrochloric, nitric, and acetic acids. Its non-volatile nature and highly stable character render it an ideal acid for many purposes. Numerous experiments have, accordingly, been carried out from time to time with a view to determining the relative rates of solution of different kinds of iron and steel in dilute sulphuric acid. Thus Burgess and Engle[1] have measured the rate of solution of electrolytic iron in both dilute sulphuric and hydrochloric acids, containing 49 and 36·5 grm. of acid respectively, per litre. As a result they find that electrolytic iron, which has not been heated, dissolves on the average four times as rapidly as steel, six times as rapidly as cast iron, and no fewer than forty times more rapidly than soft sheet iron. If the electrolytic iron has been previously heated, however, its rate of solution is enormously decreased, becoming, in fact, comparable with that of soft sheet iron. This last result is perhaps due to an alteration in the physical structure of the electrolytic iron under the influence of heat, whereby a more compact metal is obtained. From the above it is obvious that the purer the metal with which we work the slower is its rate of solution in acid, or in other words, the more highly resistant it is to acid attack.

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[1] Burgess and Engle, "Trans. Amer. Electrochem. Soc." 1906, 9, 199.

This point has been illustrated in a most remarkable manner by the American Rolling Mill Company of Middletown, Ohio, who have now placed on the market an ingot iron wonderfully free from impurity, analysis showing it to contain :—

Sulphur	0·021 per cent.
Phosphorus	0·005 ,, ,,
Carbon	0·02 ,, ,,
Manganese	Trace
Silicon	Trace
Iron (by difference)	99·954 ,, ,,
	100·000

Plates of this metal, of charcoal iron, and of ordinary steel, measuring 5 × 2·5 cm. in area and 0·2 cm. in thickness, were carefully polished and immersed completely in a 25 per cent solution of sulphuric acid contained in large beakers, at a temperature of 110° C., for a period of one and a half hours. The vessels were exposed to the ordinary diffused daylight of an American laboratory. On removing, cleaning, and weighing the plates at the conclusion of the experiments, the following results were obtained :

Metal Used.	Loss in Weight.
Steel	87·5 per cent.
Charcoal iron	52·1 ,, ,,
Pure ingot iron	2·16 ,, ,,

On examining the appearance of the metals it was observed that the surface of the steel was left rough, similar to the finest grade of emery cloth. That of the charcoal iron was very rough and pitted, while in the case of the ingot iron it was quite smooth, the tool-marks not being even obliterated.[1] The result is astonishing, and, when it has been confirmed, as undoubtedly it will be, by prolonged exposure tests to atmospheric and other corrosive influences, which tests the author understands are now in progress, there can be no doubt that the general iron consumers will rapidly learn to appreciate the value of this pure metal.

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[1] See the pamphlet which is issued by the American Rolling Mill Co. The author desires to express his hearty thanks to this firm who have

Numerous other investigations have been pursued with regard to the action of dilute sulphuric acid upon steel, but as these almost all refer directly either to the influence of certain chemical constituents purposely introduced into the steel, or else to the relative rates of corrosion of iron and steel, we shall reserve our treatment of the same until Chapters XIII and XIV, when we shall be in a position better able to do the individual authors justice.

NITRIC AND CHROMIC ACIDS.

Mention has already been made of the fact that, when iron is exposed to the action of these acids, the so-called passive state is induced. This branch of our subject receives full consideration in Chapter XII, and, for the sake of sequence, chromic acid is also alluded to in Chapter IX, in connexion with its acid salt, potassium bichromate.

BEHAVIOUR OF CAST IRON TOWARDS ACIDS.

Cast iron is a most impure form of iron, and its behaviour towards dilute and concentrated acids is, in consequence, a peculiar one, involving numerous and complicated chemical reactions and inter-reactions.

Usually when white cast iron is submitted to the action of mineral acids, heavy oils and hydrocarbons of the olefine series are produced[1] an insoluble residue of carbon and silicon, in an imperfect state of oxidation, remaining behind, together with

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kindly supplied him with the above data, together with permission to publish the same, and also with samples of iron which had been tested in the manner indicated.

[1] See Percy, "Iron and Steel," p. 144.

small quantities of chromium, titanium, tungsten, etc., if present in the original pig.

Prost[1] has studied the action of hydrochloric acid upon white pig iron, and finds that the undissolved residue varies in amount from 4 to 41 per cent, the amount being, in fact, in direct ratio to the dilution of the acid. The residue contains varying proportions of carbon, hydrogen, phosphorus, and iron, the first three increasing with the concentration of the acid, whereas the iron decreases.

When grey cast iron is dissolved in hydrochloric acid a bulky residue of graphite and partially oxidized silicon remains behind, which, on drying and warming, evolves hydrogen gas and a considerable amount of heat.[2]

When cast iron is made to dissolve slowly, as, for example, when it is exposed to the action of drainage water from mines, or to acetic acid, a change in composition takes place without a corresponding alteration in bulk or appearance. According to Calvert this peculiarity is most pronounced with acetic acid, less so with hydrochloric and sulphuric acids, while phosphoric acid is stated to have no similar action.[3]

White cast iron resists the action of acids better than mottled or grey, and is therefore usually employed in constructing the vessels used for refining gold and silver, and for many similar purposes. Coarse-grained irons and those of open texture are in general most susceptible to acid attack.

Cast iron, containing a higher percentage of phosphorus, dissolves in acid yielding a residue of phosphorus in combination with iron, insoluble in ordinary solvents. It is necessary, therefore, when estimating phosphorus in such samples, to heat the mass to redness, or to keep it at a temperature of 100° C. for over an hour in order to fully oxidize this phosphorus compound.

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[1] Prost, "Bull. Acad. roy. Belgique," 1888, p. 216. See also "J. Iron Steel Inst." 1891, I, 428.

[2] Jordan and Turner, "Trans. Chem. Soc." 1886, **49**, 219.

[3] Kohn, "Iron Manufacture," p. 65.

Cast iron rich in silicon not infrequently leaves iron silicide in the residue, from which amorphous silicon may be separated[1] on dissolving grey cast iron in either dilute sulphuric or hydrochloric acid, a residue containing sulphur is left; consequently the evolution method of estimating sulphur cannot here be employed.

Carulla[2] states that cast iron nitre pots withstand the action of sulphuric acid and nitrous and nitric acids in a glowing furnace, the seething mass taking months and sometimes years to destroy the vessel. For this power of resistance Stead[3] has given a very plausible explanation. The sulphuric acid is assumed to attack the iron to a minute extent at first, forming a protecting layer of ferrous sulphate which is insoluble in concentrated acid, and therefore preserves the metal beneath from attack.

From the foregoing remarks it will be evident that cast iron vessels, destined to resist the action of acids, should be made of the white variety. This, however, is not always convenient, particularly in those cases where toughness is required, a property in which white cast iron is well known to be deficient. In such cases the grey variety must be employed. The difficulty has been overcome in Germany,[4] however, by chilling those parts of the vessels which will come in contact with the corrosive reagents. In this way a tough, and, at the same time, highly resistant metal is obtained.

[1] Tilden, "Birm. Phil. Soc." 3, p. 203.

[2] Carulla, "J. Iron Steel Inst." 1908, I, 71.

[3] Stead, "J. Iron Steel Inst." 1908, I; 77.

[4] Lunge, "J. Iron Steel Inst." 1908, I, 84.

VIII.

THE ACTION OF ALKALIES UPON IRON.

THE action of alkalies upon the rate of corrosion of iron has received attention from quite a number of different investigators. Berzelius, the great Swedish chemist, appears to have been one of the first to draw attention to the fact that caustic alkalies preserve iron from rust; but it is only comparatively recently that any quantitative measurements with specimens of known purity have been made, and the statements to be found in literature are somewhat conflicting. The following facts, however, appear to be well established.

1. VERY DILUTE ALKALINE SOLUTIONS.

Very dilute solutions of the alkaline hydroxides do not protect iron from corrosion if exposed to the air for any length of time. Thus Cribb and Arnaud[1] found that iron rusted readily in distilled water containing small quantities of any one of the usual alkalies, as is evident from the following table into which their more important results have been condensed.[2]

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[1] Cribb and Arnaud, "Analyst," 1905, **30**, 225.

[2] The details of experimental manipulation given in Cribb and Arnaud's paper are, unfortunately, very meagre, the weight, area, and composition of the metal not being given, nor yet the volume of water used, etc. It is but fair to assume, however, that the authors carried out their experiments in such a manner as to yield results comparable amongst themselves, and in so far as this was the case, they are of value. It is to be hoped that, in future communications to scientific journals, authors will be careful to give all the important details necessary to render their work comparable with that of other investigators and hence of permanent value.

Action of Dilute Alkaline Solutions upon Iron during Twenty-four Hours.

Alkali Used.	Parts of Alkali by Weight in 100,000 Parts of Water.	Corrosion at Room Temp. Expressed as Mg . Fe_2O_3.	Corrosion at 100° C. Expressed as Mg . Fe_2O_3.
Sodium hydroxide ($NaOH$).	4	7·0	18·5
	10	2·8	19·3
	20	0·0	5·8
	40	0·0	0·0
Potassium hydroxide (KOH).	5·6	5·8	13·7
	14·0	0·0	12·8
	28·0	0·0	0·0
Ammonium hydroxide (NH_4OH)	17·0	5·0	11·5
	34·0	0·0	0·0
Calcium hydroxide ($Ca[OH]_2$)	9·25	7·5	20·5
	18·5	5·0	3·5
	27·75	0·0	0·0
Barium hydroxide ($Ba[OH]_2$)	8·55	5·2	14·4
	21·37	0·0	11·3
	42·74	0·0	0·0

These results are of considerable importance, for they show that, contrary to the generally accepted ideas, dilute solutions of the alkaline hydroxides are incapable of entirely preventing the corrosion of iron exposed to the ordinary atmosphere, until a certain "limiting concentration" of the alkali has been reached. Beyond this point corrosion does not take place. We further see that the value of the limiting concentration is a function of the temperature, increasing rapidly with the same.

The scientific explanation for the above is not far to seek. On exposure to the air, the alkalies rapidly absorb carbon dioxide yielding carbonates. Consequently we are not here dealing so much with the action of pure alkaline hydroxide solutions upon iron as with that of mixtures of these and of their carbonates, the proportion of the latter clearly depending upon the length of exposure and percentage of carbon dioxide in the atmosphere. If these are great the hydroxides may be completely converted into their corresponding carbonates. As we shall see in the next chapter, carbonates of even the alkali metals, sodium and potassium, cannot inhibit corrosion entirely until a certain limiting concentration has been reached, the value for which varies for each particular metal. It is easy to understand, therefore, that, unless the concentration of the free alkalies be such that, on conversion into their carbonates, the limiting concentration of the latter has been reached or exceeded, corrosion must eventually proceed on prolonged exposure to air. The time during which such dilute hydroxide solutions can protect the iron is obviously a measure of the rate at which carbon dioxide is being absorbed, and the value obtained for the limiting concentration of the hydroxides will vary according to the time of exposure and the local conditions obtaining during the course of the experiments.

More recently Heyn and Bauer[1] have studied the action of dilute solutions of the hydroxides of calcium and sodium upon iron plates, measuring 4·5 × 3 cm. in area, and exposed to the atmosphere for a period of twenty-two days, that is twenty-two times as long as the metal used by Cribb and Arnaud. Friend has determined the limiting value of potash solutions containing iron, measuring 4 × 5 cm. in area, and exposed to the atmosphere of a chemical laboratory for a whole month, that is twenty-eight times as long as in Cribb and Arnaud's experiments. The values obtained for the limiting concentrations are consequently proportionately greater, as is evident from the following table :—

Alkali.	Limiting Concentration, Expressed as Grm. per Litre Lies Between the Following Values :—		
	(Cribb and Arnaud.) 24 Hours.	(Heyn and Bauer.) 22 Days.	(Friend.) 28 Days.
Sodium hydroxide NaOH.	0·10 and 0·20	1·0 and 10·0	—
Calcium hydroxide $Ca[OH]_2$.	0·185 and 0·278	0·18 and 0·89	—
Potassium hydroxide KOH.	0·056 and 0·14	—	1·1 and 2·8

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1908, **26**, 2.

In perfectly pure alkaline solutions, free from carbonate and other impurities, iron will not rust even though the solutions are excessively dilute. This has been clearly demonstrated by Friend, who employed the apparatus shown in Fig. 10 (p. 58). A piece of pure iron foil and 100 c.c. of three times normal potassium hydroxide solution[1] were introduced into B and, after the pressure of the air had been reduced to about 3 cm. of mercury, the vessel was hermetically sealed. The potash solution was prepared as free from carbonate as possible, and, after shaking thoroughly in order to ensure the absorption of every trace of carbon dioxide from the air, walls of the vessel, and surface of the iron, the last-named was rinsed into A and the solution poured back into B. Bulb A was now cooled by a stream of cold water whilst B was gently warmed in a hot-water bath. When about 30 c.c. of water had distilled into A, the hot-water bath was removed and, after shaking gently to wash the sides of A, the liquid was poured back into B. The distillation was repeated, but this time, when A contained some 30 c.c. of water, the vessel was placed in a corner of the laboratory, exposed to the diffused sunlight, where it remained undisturbed for a period of twelve days. At the end of this period the metal was found to be perfectly free from rust, and exhibited as high a degree of polish as on the day on which the experiment was begun. The vessel was now opened, and the alkali in A estimated by titration with dilute hydrochloric acid solution using phenol phthalein as indicator. The result showed that the liquid was $\frac{1}{856}$ normal, that is, it contained 6·5 parts by weight of caustic potash in 100,000 parts of water. Owing to the difference in vapour pressure between the concentrated potash solution in B and the dilute liquid in A, the latter was reduced to two-thirds of its original volume during the twelve days of rest, the missing third having slowly distilled over as pure water into B. Consequently at the beginning of the experiment the concentration of the alkali would be of the order of 4·5 parts of potash in 100,000 parts of water. These results may be taken as proving, therefore, that very dilute alkaline hydroxides do not effect the corrosion of iron when exposed to pure atmospheres.

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[1] That is, a solution containing 168 grm. of hydroxide, KOH, per litre.

STRONG SOLUTIONS OF THE ALKALIES.

Moderately strong solutions of caustic alkalies preserve iron from corrosion at ordinary temperatures for an indefinite time. The experiments of Cribb and Arnaud, to which reference has already been made in the preceding section, show that such is the case for twenty-four hours at any rate, when the concentration of the alkali exceeds a certain limit. It is impossible to ascertain, however, from the meagre details given, to what degree of accuracy their results could be relied upon.

Heyn and Bauer,[1] and Friend, have investigated the case for several alkalies, and these we may proceed to consider individually.

Calcium Hydroxide.—Heyn and Bauer suspended a series of iron plates, measuring 3 × 4·5 cm. in area, by means of bent glass rods, in various concentrations of calcium hydroxide solutions for a period of twenty-two days. At the end of this time the plates were removed, washed, cleaned and weighed. The results are given in the following table, being the mean of two sets of experiments.

Grm. of CaO per Litre.	Duration of Experiment. Days.	Loss in Lot in Grm.
0·0	22	0·0646
0·67	22	0·0000
1·35 (saturated)	22	0·0000

Sodium Hydroxide.—The results given in the following table were arrived at by Heyn and Bauer in an exactly similar manner to the preceding:—

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1908, **26**, 2.

Grm. of NaOH per Litre.	Duration of Experiment. Days.	Loss in Weight in Grm.
0·0	22	0·0653
10	22	0·0002
100	22	0·0005
Saturated	22	0·0002

Potassium Hydroxide.—Friend immersed pieces of pure iron foil, measuring 5 × 4 cm. in area, in resistance glass beakers, the four corners of the metal resting in contact with the sides and bottom of the containing vessel. The results obtained are given in the following table:—

Grm. of KOH per Litre.	Duration of Experiment. Days.	Loss in Weight in Grm.
0·0	28	0·0685
2·8	28	0·0000
28	28	0·0001
168	28	0·0003
Saturated	21	0·0002

No quantitative data are to hand for the action of ammoniacal solutions upon iron, other than those of Cribb and Arnaud already quoted. Pennock and Morton[1] state that iron does not rust in concentrated aqueous solutions of ammonia, although they find that freshly rusted moist iron is attacked by the same. Friend has kept strips of pure iron in contact with air and $\frac{1}{30}$ normal ammonium hydroxide solutions in sealed tubes for several years without the slightest change in appearance being observable.

The conclusions to be drawn from all these experiments are sufficiently obvious and need no further comment. Since lime is comparatively cheap, and is much less violent in its general chemical reactions than either sodium or potassium hydroxide, its use is to be recommended in the prevention of the rusting of iron whenever possible. The fact that the addition of 5 per cent of this material to boggy, sour land has been found by Cushman to exert a very marked retarding action upon the corrosion of iron work embedded in it,[1] is therefore not to be wondered at.

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[1] Pennock and Morton, "J. Amer. Chem. Soc." 1902, **24**, 377.

Carulla[2] has drawn attention to the fact that cast-iron stills for ammonia prove everlasting. One such had been under his observation for eighteen years, and was as sound and perfect as when erected. The reactions taking place in these stills were, of course, entirely basic, lime being used to expel the fixed portion of the alkali. Kempson and Co. are able to confirm this from their experience.[3]

Since, during the process of ordinary coal-gas manufacture, a small amount of ammonia invariably escapes through the scrubbers into the gasholders, along with the gas, the water in the bottom of the gasholders gradually assumes an alkaline reaction. It seemed of interest to inquire, therefore, to what extent this alkalinity would retard the corrosion of those parts of the gasholders which are more or less completely immersed in the water. To this end Friend obtained some water from the smallest and oldest gasholder in the Darlington Gas Works, the capacity of the well being approximately 30,000 gallons. Analysis, prosecuted by W. West, showed the liquid contained 0·0088 per cent of free ammonia, and 0·0045 per cent of fixed. Pure iron plates, measuring 3 × 5 cm. in area, were then immersed, each in 100 c.c. of this liquor, for a period of eight days, at the end of which time the loss in weight was determined. Similar plates were exposed for a like period to the action of tap water, and of the liquor diluted with tap water saturated with Darlington coal-gas, in order to render the conditions as comparable as possible. The results obtained were as follows:—

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[1] See "J. Iron and Steel Inst." 1909, I, 33.

[2] Carulla, "J. Iron Steel Inst." 1908, I, 71.

[3] Kempson and Co., "J. Iron Steel Inst." 1908, I, 83.

Liquid Used.	Loss in Weight in Grm.
100 c.c. Tap water	0·0242
100 c.c. Tap water, saturated with coal-gas	0·0208
80 c.c. Tap water, saturated with coal-gas, and 20 c.c. Gasholder liquid	0·0178
50 c.c. Tap water, saturated with coal-gas, and 50 c.c. Gasholder liquid	0·0144
100 c.c. Gasholder liquid	0·0130

These results show very clearly that, as far as the useful life of the gasholder is concerned, it is to the advantage of the gasworks officials to renew the water in the wells of their gasholders as seldom as possible.

3. FUSED ALKALINE HYDROXIDES.

Fused caustic alkalies are highly corrosive towards iron. This is particularly true of caustic soda under pressure, and the corrosion is aggravated on still further increasing the temperature. It would appear that wrought iron suffers more than cast iron under these conditions.[1] According to Groves [2] solid caustic potash, containing 5 per cent of water, when fused at a gentle heat, readily attacks steel, whereas the action of caustic soda in similar circumstances is much less.[3]

As far as the present author is aware, however, no reliable quantitative data have been published on these points.

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[1] Scheurer Kestner, "Bull. Soc. Chim." 1897, **15** (3), 1250.

[2] Groves, "Proc. Chem. Soc." 1903, **19**, 158.

[3] Compare Venator, "Chemiker Zeitung," 1886, **10**, 319, 380.

IX.

THE INFLUENCE OF AQUEOUS SOLUTIONS OF SINGLE SALTS UPON IRON.

For many years it has been a matter of common knowledge that the presence of soluble metallic salts dissolved in the water in contact with iron has a marked influence upon the rate of corrosion. Thus, for example, whilst iron may be kept perfectly bright and free from rust for an indefinite time in contact with strong solutions of sodium carbonate or potassium chromate, yet when immersed in sea water, which is essentially an aqueous solution of sodium and magnesium chlorides, corrosion takes place with markedly greater rapidity than in pure water alone. Many chemists, therefore, have busied themselves from time to time in endeavouring to determine the relative corrosive actions of different salts and of mineral waters containing dissolved salts upon iron and steel.[1]

Until very recently, however, the results obtained, although interesting by themselves, did not admit of the deduction of any general conclusions or laws from them, on account of the very variable nature of the conditions under which the experiments were carried out. Furthermore, the value of many of these researches is considerably reduced, because even these variable conditions, amongst which may be classed concentration and temperature, being regarded as relatively unimportant, are not described in sufficient detail, and in a few cases not even alluded to at all. Consequently, both repetition of the experiments and comparison of the results with those of other investigators are rendered impossible. The great need, therefore, has been for a thorough investigation of the relative corrosive actions of solutions of electrolytes upon iron under a series of well-defined conditions, rather than for an accumulation of isolated facts, applying only in exceptional circumstances seldom met with in actual practice.

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[1] Wagner, "Dingler's Poly. J." 1875, **218**, 70; 1876, **221**, 260.

Calvert, "Chem. News," 1871, **23**, 98.

Lunge, "J. Iron Steel Inst." 1886, I, 386; from "Chemisches Repertorium," **10**, 86.

Menke, "Compt. rend." 1887, **104**, 1800.

Petit, "Compt. rend." 1896, **122**, 1278.

Senderens, "Bull. Soc. Chim." 1897, **15**, 691.

Moody, "Proc. Chem. Soc." 1903, **19**, 157, 239.

Dunstan, "Proc. Chem. Soc." 1903, **19**, 150.

Raikow, "Chem. Zeitung," 1903, **27**, 1192.

Until quite recently no one had attempted to meet this need, and we cannot wonder that the greatest confusion should have arisen in the minds of experts on the whole question; and a search through textbooks and the original literature of scientific journals shows only too clearly how ignorant we are of the working of many of the commonest and apparently the simplest corrosive agencies.

One of the greatest mistakes which chemists have made all along the line lies in the assumption that, because for any one concentration a number of solutions of different salts can be arranged in order of increasing corrosivity, therefore the same order will be preserved for any and all other concentrations of the same salts under like conditions. Furthermore, it has generally been accepted that, because solutions of certain salts of one particular strength will inhibit the corrosion of iron, the same is true for all other strengths.

Mugdan, "Zeit. Elektrochem." 1903, **9**, 442.

Lindet, "Compt. rend." 1904, **139**, 859.

Cribb and Arnaud, "Analyst," 1905, **30**, 225.

Dunstan, Jowett, and Goulding, "Trans. Chem. Soc." 1905, **87**, 1558.

Menzel, "J. Iron Steel Inst." 1907, III, 522.

Grossmann, "J. Iron Steel Inst." 1909, I, 668; from "Engineer," **107**, 262.

Rohland, "Zeit. Elektrochem." 1909, **15**, 865.

But such assumptions are quite unwarrantable. For example, solutions of common salt in water are known to be particularly corrosive in their action upon iron. But as early as 1845, Adie[1] drew attention to the remarkable fact that saturated solutions of common salt exhibit a pronounced tendency to inhibit corrosion, which is the exact reverse. Chemists, however, are not generally aware of this discovery, although the truth of the same is now beyond dispute, as we shall presently see.

Nearly three years ago, however, a flood of light was thrown upon the whole question by the very thorough and extensive researches of Professors Heyn and Bauer, and since then a few other investigators have enriched the leading scientific journals with contributions on the same and kindred subjects.

I. SINGLE ELECTROLYTES AT ROOM TEMPERATURE.

In order to investigate the action of solutions of single salts upon iron at the temperature of the room, Heyn and Bauer,[2] suspended carefully weighed and polished iron and steel plates, measuring 4·5 × 3 cm. in area, by means of glass tubes in glass cylinders as shown in Fig. 28. In this way a vertical suspension was assured at an accurately known depth below the surface of the liquid, and any disturbing influences arising from contact of the metal with the sides and bottom of the containing vessel were thereby entirely avoided. Two kinds of metal were used, namely wrought iron and mild steel, the analyses being as follows :—

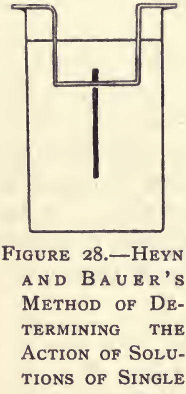

FIGURE 28.—HEYN AND BAUER'S METHOD OF DETERMINING THE ACTION OF SOLUTIONS OF SINGLE SALTS UPON IRON.

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[1] Adie, "Min. Proc. Inst. Civil Engineers," 1845, **4**, 323. See also Lunge, "Dingler's Polytech. J." 1886, **261**, 131.

[2] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Materialprüfungsamt, Berlin; 1910, **28**, 62; 1908, **26**, 2.

	Wrought Iron. Per cent.	Mild Steel. Per cent.
Carbon	0·104	0·04
Silicon	—	0·01
Manganese	0·600	0·59
Phosphorus	0·173	0·034
Sulphur	0·099	0·025
Copper	0·239	0·16
Arsenic	0·019	—
Iron (by difference)	98·766	99·141
	100·000	100·000

It is almost a pity that these investigators did not use a purer form of metal, as some of the constituents possibly were the cause of certain peculiar results obtained which, as we shall see later, Friend has been unable to confirm.

The glass containing-vessels were filled with series of solutions of various electrolytic salts in water, the concentration of each salt ranging in regular gradations from distilled water (that is m/∞ where m stands for the molecular weight) to solutions saturated at room temperature, namely 16°-21° C. In the last-named case excess of the salt always lay at the bottom of the vessels. No special precautions were taken in order to remove carbon dioxide and other gaseous impurities from the air to which the whole was exposed, except in a few cases when it seemed probable that a disturbing influence might be exerted by them upon the course of the experiment. At the end of twenty-two days, during which time the metal was allowed to remain entirely undisturbed, the iron plates were removed, polished, washed with alcohol and again weighed, any loss in weight being regarded as a measure of the corrosion.

Friend and Brown,[1] on the other hand, employed small plates of Kahlbaum's pure iron foil, measuring 5 × 4 cm. in area. These were carefully polished with emery paper, and immersed in resistance glass beakers containing 100 c.c. of the solution to be tested, in such a manner that the four corners of the plates rested in contact with the sides and bottom of the beaker, as shown in Fig. 29.

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[1] Paper entitled "The Action of Aqueous Solutions of Single and Mixed Electrolytes upon Iron" read before the Iron and Steel Institute, London, 11 May, 1911.

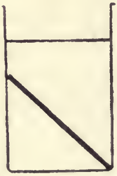

FIGURE 29.—FRIEND AND BROWN'S METHOD OF DETERMINING THE ACTION OF SINGLE SALT SOLUTIONS UPON IRON.

Each series of these beakers was carefully protected from dust by enclosure under a large glass bell jar, so arranged as to admit a plentiful supply of air and, at the same time, to allow of uniform illumination—a factor which we have in a previous chapter seen to be of great importance. The whole was placed on a bench in the laboratory, some distance away from the window, in such a manner that only diffused daylight could ever shine upon the beakers. After fourteen days the metal was removed, cleaned, and weighed.

For the sake of convenience we may divide the salts studied into two groups, according as their concentrated solutions are capable or otherwise of inhibiting the corrosion of iron.

GROUP I.—ELECTROLYTES WHICH YIELD LIMITING SOLUTIONS.

The curve BCDE (Fig. 30), which is that given by Heyn and Bauer as representing the corrosive action of potassium ferrocyanide, and may be regarded as typical of this group. The point B represents the effect of distilled water alone upon iron, and F the concentration at which the solution becomes saturated with the salt at the temperature of the room.

When present in very small quantities, such as, for example, 0·001 to 0·1 grm. per litre, the majority of the salts were found to exert a slight retarding action upon the corrosion of the iron. This is represented by the fall BC in the curve. This phenomenon was not observed in every case, but that may be due to the retarding action occurring at still smaller concentrations in such cases than were convenient to employ. On the other hand it is not easy to see why any such action should occur at all. Further increase in the concentration of the salt results in an increased corrosive action, as indicated by the rise in the curve CD. At D a maximum is reached, which in general considerably exceeds that of distilled water alone, and the salt is said to be at its "critical" concentration. From this point onwards the curve falls once more, striking the abscissa at E, which gives the "limiting concentration". From E to F no corrosion occurs, and iron may be kept for indefinite periods in contact with air and such solutions without undergoing any appreciable corrosion.

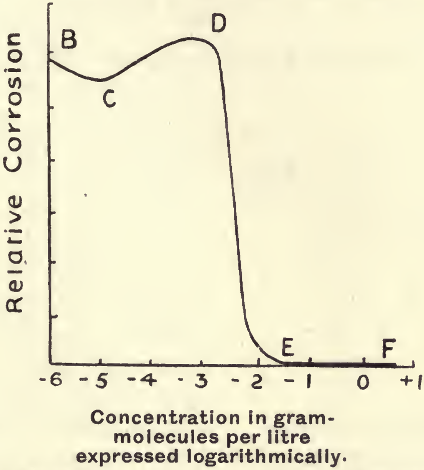

FIGURE 30.—CURVE REPRESENTING THE CORROSIVE ACTION OF SOLUTIONS OF POTASSIUM FERROCYANIDE. (HEYN AND BAUER).

It was found in general that, in the neighbourhood of the critical concentration, the iron was locally attacked with vigour, but the corroded areas were very unequally distributed over the surface of the metal. It is very probable that this is due to the presence of impurities in the metal, irregularly distributed throughout its mass, whereby local galvanic activity is induced in a manner explained in a succeeding chapter.[1]

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[1] See Chapter XIV.

All the electrolytes belonging to this group, which have as yet been studied, are given in the following table, together with their critical and limiting concentrations. These latter are only approximate, save in one or two isolated cases, for their accurate determination would involve a tremendous amount of work. Fortunately this is not necessary. Furthermore the values are extremely variable, depending to a large extent upon the areas of the exposed iron, the intensity of illumination, and a variety of other factors.

The results obtained for the carbonates of sodium and potassium are interesting (Fig. 31), as illustrating the fact that solutions of these salts containing about one grm. per litre are some 50 per cent more corrosive than distilled water alone. That saturated solutions of the alkaline carbonates completely prevent the corrosion of iron immersed in them has been known for very many years, as the writings of Payen[1] Mallet[2] and Adie[3] testify. More than twenty years ago Menke[4] recommended the employment of potassium carbonate as a preservative against the corrosion of boiler plates. Failing this, the carbonate of sodium was suggested as being cheaper if somewhat less efficient.

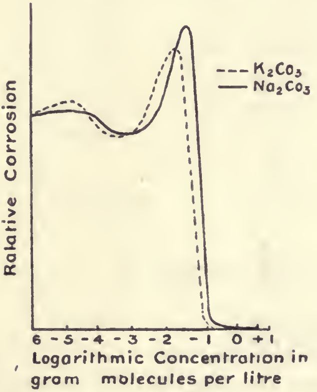

FIGURE 31.—CURVES SHOWING THE RELATIVE CORROSION OF IRON PLATES IMMERSED IN VARYING CONCENTRATIONS OF ALKALI CARBONATES. (HEYN AND BAUER).

That dilute solutions of these salts, however, stimulate cor-

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[1] Payen, "Compt. rend." February, 1837.

[2] Mallet, "British Association Reports," 1838, p. 253.

[3] Adie, "Min. Proc. Inst. Civil Engineers," 1845, 4, 323.

[4] Menke, "Compt. rend." 1887, 104, 1800.

ELECTROLYTES OF GROUP I SHOWING THEIR CRITICAL AND LIMITING CONCENTRATIONS.[1]

Metal Used.	Electrolyte.	Critical Concentration. Grm. per Litre. (Approx.)	Limiting Concentration in Grm. per Litre Lies Between—	Remarks.
Wrought [3]	$K_4FeC_6N_6$	**0·1**	1 to 2	
Kahlbaum's foil [4]	$K_4FeC_6N_6$	**0·2**	—	
Wrought [3]	$K_3FeC_6N_6$	**0·1**	1 to 2	
,,	$KMnO_4$	**0·1**	0·1 ,, 1·0	
,,	K_2CO_3	**1·0**	1 ,, 10	
,,	KIO_3	**0·01**	0·1 ,, 1·0	Do not afford complete protection after limiting concentration reached.
,,	KCN	**0·1**	0·1 ,, 1·0	
,,	$KBrO_3$	**0·1**	0·1 ,, 1·0	
,,	$KClO_3$	**0·1**	74·5	Limiting concentration and saturation point practically coincident.
Steel [3]	$CaCl_2$	1·27	510	
,,	$Na_2S.9H_2O$	0·1	100	
Wrought [3]	$NaHCO_3$	1·0	1 to 10	
,,	Na_2CO_3	**1·0**	1 ,, 10	
—[2]	Na_2CO_3	0·795	1·06 ,, 1·59	
Wrought [3]	$Na_2B_4O_7.10H_2O$	**0·1**	1 ,, 10	
,,	$Na_2H.PO_4.12H_2O$	**1·0**	1 ,, 10	
,,	$CH_3 \cdot COONH_4$	**0·01**	0·1 ,, 1·0	Iron visibly attacked in conc. solution.
,,	$(NH_4)_2HPO_4$	**0·01**	1·0 ,, 10	
,,	CrO_3	—	0·01 ,, 0·05	Render iron passive. Full discussion, Chapter XII.
Kahlbaum's pure iron foil.[4]	CrO_3	—	0·056	
Wrought [3]	K_2CrO_4	—	0·01 to 0·1	
,,	$K_2Cr_2O_7$	—	0·01 ,, 0·1	
—[5]	$K_2Cr_2O_7$	—	0·076	
Kahlbaum's pure foil.[4]	$K_2Cr_2O_7$	—	0·084	

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[1] Except where otherwise stated these numbers are taken from the experimental data supplied by Heyn and Bauer in the two memoirs to which reference has already been made.

[2] Cribb and Arnaud, "Analyst," 1905, **30**, 225; iron of unknown composition.

[3] "Analysis," p. 129.

[4] Friend, "J. Iron Steel Inst." 1911, in the Press.

[5] Cushman, "Bulletin No. 30," U.S. Department of Agriculture, Washington, 1907.

[6] Figures in bold type signify that at the critical concentration the corrosive action is greater than that of distilled water.

rosion more actively than distilled water is a point not generally realized, although Payen, in the memoir referred to above, calls attention to it. Cribb and Arnaud[1] rediscovered[2] the fact in 1905 and made a few quantitative experiments with sodium carbonate solution. Their results are given in the Table along with those of Heyn and Bauer, and the reader will observe the general agreement between the two, the numerical values for the critical concentrations being almost identical in the two cases.

The practical importance of these observations will be at once evident when we remember that feed waters for boilers are frequently rendered slightly alkaline during the process of softening. Although the concentration of the carbonate may be very small at first and thus exert no appreciable influence upon the corrosive power of the water, it will soon be increased by the escape of steam from the boiler and thus be brought to a strength which can stimulate the corrosion of the metal to a very pronounced extent. Were it impossible for air to gain access to the boiler, this increase in the concentration of the carbonate would be a matter of small importance, but air enters with the feed water, and the results may, and often do, prove serious.

Fortunately we have, on the other hand, a number of counteracting influences tending to ameliorate the case, among which are the following :—

1. The concentration of the alkaline carbonate will not necessarily remain at its critical value; in fact, the probability is that it will soon exceed it and tend to approach the limiting value, a marked reduction in the corrosion following in its wake. Such a desirable condition of affairs may of course be artificially

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[1] Cribb and Arnaud, "Analyst," 1905, **30**, 225.

[2] It is evident from the manner in which these investigators describe their results that they were not acquainted with the early literature on this subject, and regarded their observation as entirely new; and so far as the present author can gather from the wording employed in Heyn and Bauer's two memoirs, even these investigators were unacquainted with the writings of Payen and Mallet upon this point.

brought on by following Menke's suggestion, and introducing quantities of sodium or potassium carbonate. The amounts, however, must be sufficiently great, so as to exceed the critical concentration, otherwise, if the waters are only very faintly alkaline, more harm may be done than good.

2. The majority of softened waters yield a deposit when heated, which covers the plates and tubes, and thus serves as a fairly efficient protective coating towards the metal underneath.

3. The boilers being dark inside will corrode considerably less rapidly than if exposed to the stimulating action of light,[1] and experiments performed in a well-lighted laboratory may for this reason greatly exaggerate the actual state of affairs in practice unless due allowance is made for the difference.

Returning, now, to the other members of this group of salts, it would appear from the experiments of Heyn and Bauer that the chlorate, bromate, iodate, and cyanide of potassium do not afford complete protection against corrosion between the points E and F (Fig. 30, p. 131), a few specks of rust always appearing. The action, however, was very minute, having an almost inappreciable effect upon the weight of the metal used.

The behaviour of diammonium hydrogen phosphate, $(NH_4)_2HPO_4$, is remarkable, as a glance at Fig. 32 will show. Up to the limiting concentration it reacts in a normal manner. Before saturation is reached, however, corrosion begins again. But it is not rusting in the ordinary sense of the term. On immersion in the saturated solution the iron became covered with gas bubbles and, after a few hours, appeared considerably duller, becoming finally coated with a greyish green deposit.

In the case of potassium chlorate (Fig. 33), calcium chloride, and sodium sulphide, points E and F (Fig. 30, p. 131) are practically coincident, that is to say, the limiting concentration is a saturated solution of the salt.

A few electrolytes of this group apparently yield no critical concentrations. These are chromic acid and its two potassium salts, all of which are well known to be powerful passivifiers. It may, of course, happen that the critical concentrations are intermediate between any two employed by the different investigators. The action of chromic acid is interesting. Reference to the curve in Fig. 34 shows that, in the immediate neighbourhood on the right of the limiting concentration, solutions of the acid have no appreciable solvent action upon the iron, which metal is protected by them from corrosion for indefinite periods of time, remaining quite bright and seemingly unaltered. Probably, however, an excessively slow process of solution is going on, which only becomes perceptible after many months. As the concentration of the chromic acid increases, the iron begins to lose perceptibly in weight, becoming darker and ultimately almost black in appearance. From the results given by Heyn and Bauer one might conclude that solutions of potassium bichromate behave in an analogous manner. The loss in weight of the metal observed by these investigators, however, was probably due to the solution of

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[1] See pp. 90-93.

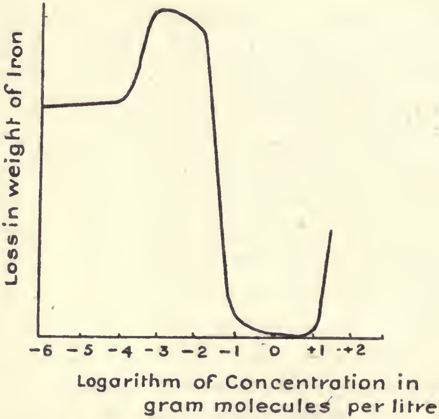
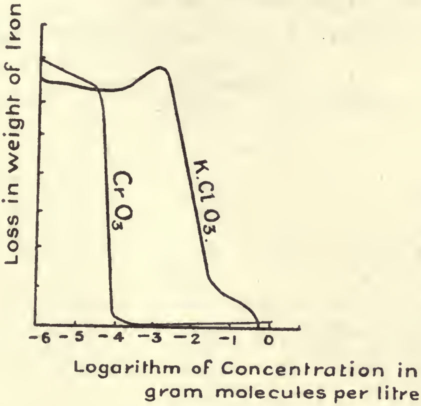


FIGURE 32.—HEYN AND BAUER'S CURVE SHOWING THE RELATIVE CORROSIVE ACTION OF VARIOUS CONCENTRATIONS OF DIAMMONIUM HYDROGEN PHOSPHATE.

manganese which analysis (p. 129) showed the metal to contain, for, as Cushman was the first to point out, the measure of the solubility of pure iron in concentrated solutions of potassium bichromate is too minute to be detected in the course of a few weeks, whereas iron containing manganese readily loses in weight.[1]



FIGURES 33 AND 34.—HEYN AND BAUER'S RESULTS FOR THE CORROSIVE ACTION OF SOLUTIONS OF POTASSIUM CHLORATE, AND OF CHROMIC ACID.

GROUP II.—ELECTROLYTES WITH IMAGINARY LIMITING SOLUTIONS.

Attention has already been drawn to the fact that, for solutions of potassium chlorate, calcium chloride, and sodium sulphide, points E and F (Fig. 30, p. 131) are practically coincident, the limiting concentration of each salt being a saturated solution of the same. We now pass on to consider the case of those salts in which F lies to the left of E, that is to say, their saturated solutions are incapable of inhibiting corrosion. The limiting solution cannot, therefore, be reached, and its value becomes imaginary, for further addition of crystals of the salt to the liquid can have no effect. This group contains by far the larger number of electrolytes, the following table giving a complete list of all those which have as yet been studied, although it is far from exhaustive. The approximate values of the critical concentrations are also given. The figures in bold type in the third column signify that at the critical concentration the solutions are more corrosive than distilled water alone, according to the authority quoted.

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[1] This branch of our subject is fully discussed in Chapter XII, where the whole subject of passivity is dealt with.

ELECTROLYTES OF GROUP II, SHOWING THEIR CRITICAL CONCENTRATIONS.

Iron Used.	Electrolyte.	Critical Conc. in Grm. per Litre. (Approx.)	Authority.
W[1]	KCl	50	Heyn and Bauer
K[2]	KCl	**5**[3]	Friend
W	K_2SO_4	10	Heyn and Bauer
K	K_2SO_4	**10**	Friend and Brown
,,	KNO_3	**1-15**	,,
W	NaCl	10·05	Heyn and Bauer
K	NaCl	**5**	Friend and Brown
W	$Na_2SO_4.10H_2O$	10	Heyn and Bauer
K	$Na_2SO_4.10H_2O$	**10**	Friend and Brown
W	$NaNO_3$	**0·1** **50**	Heyn and Bauer
K	$NaNO_3$	**50**	Friend and Brown
W	$CaH_2(CO_3)_2$	0·14	Heyn and Bauer
,,	$CaSO_4$	2·034	,,
S[1]	CaS	**0·0014**[4]	,,
W	$BaCl_2.2H_2O$	100	,,
K	$BaCl_2.2H_2O$	**10**	Friend and Brown
W	$FeSO_4.7H_2O$	**100**	Heyn and Bauer
,,	As_2O_3	**0·064**	,,
,,	$MgCl_2.6H_2O$	**100**	,,
K	$MgCl_2.6H_2O$	**20**	Friend and Brown
W	$MgSO_4.7H_2O$	**10-50**	Heyn and Bauer
K	$MgSO_4.7H_2O$	**10-50**	Friend and Brown
W	$MnSO_4.5H_2O$	**0·1**	Heyn and Bauer
,,	NH_4CNS	**0·01**	,,
,,	NH_4Cl	**100**	,,
,,	$(NH_4)_2SO_4$	**200**	,,
,,	NH_4NO_3	**500**	,,

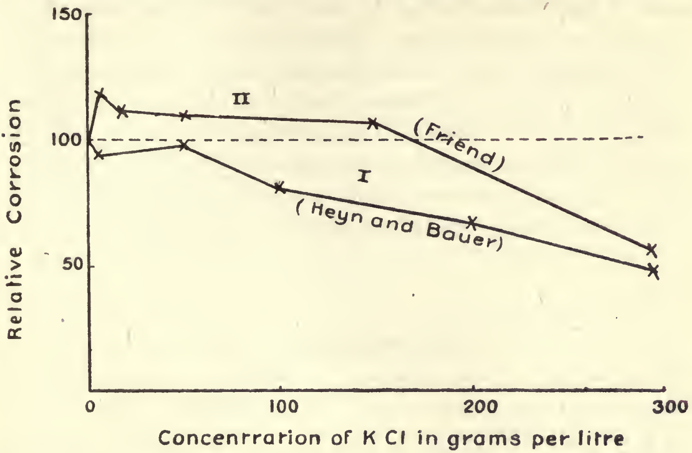
[1] The symbols W and S refer to wrought iron and steel used by Heyn and Bauer, analyses of which are given on p. 129.

[2] The symbol K refers to Kahlbaum's pure iron foil.

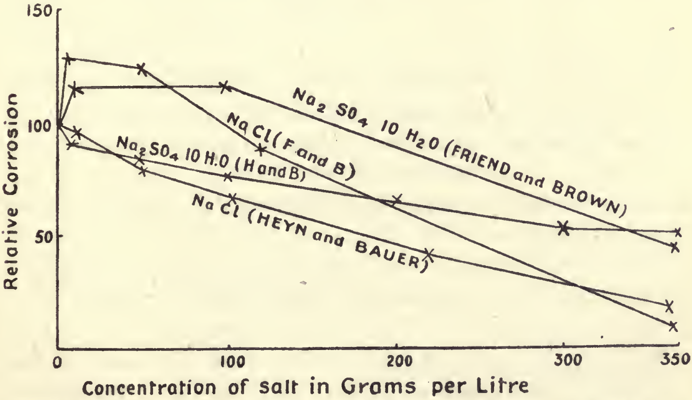
[3] The numbers in bold type signify that at the critical concentration the corrosive action is greater than that found for distilled water alone.

[4] This is calculated according to the formula CaS, for Heyn and Bauer give their results for this body in grms. of calcium per litre, which is no doubt more exact. For the sake of uniformity, however, the author prefers this method.

The results obtained for the sulphates and chlorides of

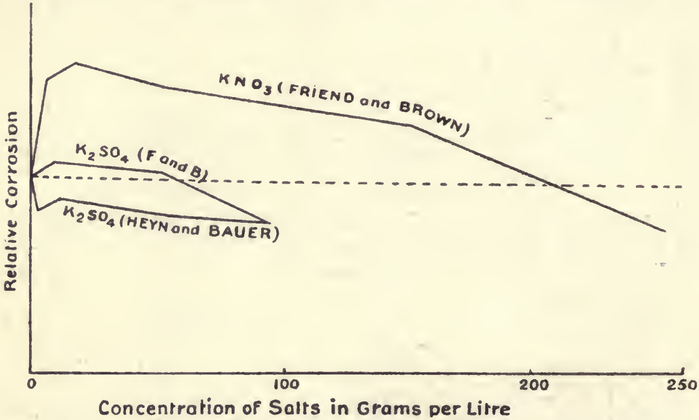


Figures 35 and 36.—The Corrosive Action of Potassium Chloride Solutions as Determined by Heyn and Bauer, and by Friend and Brown.



Figures 37 and 38.—The Corrosive Action of Solutions of Sodium Sulphate and Chloride.

sodium and potassium are shown graphically in Figs. 36, 37, 38, and 39. That fairly strong solutions of these salts retard the corrosion of iron is a fact not generally realized by chemists, who regard the chlorides, at any rate, as being particularly corrosive in their behaviour. Nevertheless, the inhibiting action of concentrated brine was emphasized nearly seventy years ago by Adie,[1] whose contributions to the subject seem to have been generally overlooked. This investigator immersed weighed pieces of cast and wrought iron separately both in fresh water and in saturated sodium chloride solution, and left them for a number of days exposed to the air. At the conclusion of the experiment the metals were weighed, the following results being obtained :—



FIGURES 39 AND 40.—THE CORROSIVE ACTION OF SOLUTIONS OF POTASSIUM SULPHATE AND NITRATE.

Conditions of the Experiments.	Loss in Fresh Water. (Grains).	Loss in Salt Water. (Grains).
20 pieces of wrought iron weighing 374 grains, exposed for 80 days	1·9	0·1
3 rods of cast iron weighing 787 grains, exposed for 62 days	1·6	0·4

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[1] Adie, " Min. Proc. Inst. Civil Engineers," 1845, 4, 323.

The wrought iron thus corroded nineteen times as much in fresh water as in salt solution, and the cast iron four times as much, during the periods stated.

Adie explained these on the ground of the decreased solubility of oxygen in salt solutions, and supported his arguments by a few determinations of the solubility of oxygen in different liquids. As we shall see later on, this is undoubtedly the correct explanation.

Now although chemists have been slow to accept these results, marine engineers have accepted them because they are in harmony with their own experience. The rusting of boilers has not infrequently been arrested by increasing the amount of their sea water content without altering any of the other conditions of working. Rowan[1] quotes the case of a steamer whose boilers were "worked fresh," that is to say with a minimum proportion of sea water. In a little more than a twelvemonth from the start, a new set of boilers was required. These were duly inserted, and from that time forward the proportion of sea water was considerably increased, with the result that the life of the boilers was greatly prolonged.

It will be observed that, according to the researches of Heyn and Bauer, as indicated in the curves plotted in Figs. 36-39, even dilute solutions of the chlorides and sulphates of potassium and sodium have less corrosive influences than distilled water alone—a result which is contrary to experience. Heyn and Bauer themselves note it as unusual, and the experiments of Friend and Brown, carried out with pure iron foil, and shown graphically in the same figures, support the general opinion. The reason for this it is very difficult to find, and the very fact that careful investigators can arrive at such opposite conclusions shows how essential it is that great care be taken in drawing conclusions of moment from a limited series of observations.

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[1] Rowan, "British Association Reports," 1876. See also Rowan, "The Practical Physics of the Steam Boiler," published by King & Son, 1903, Chapter VII.

The balance of evidence appears to lie in favour of the work of Friend and Brown, since their metal was much purer, and their results are more in accord with the practical experience of engineers, and the qualitative observations of numerous other investigators. Further than this, however, we cannot safely go.[1]

In the absence of air, solutions of the sulphates and chlorides of the alkali metals appear to have no action upon pure iron. Adie[2] was probably the first to show this qualitatively in the case of sodium chloride. Friend has more recently studied the question quantitatively. Strips of pure iron foil, measuring 4·7 × 1·3 cm. in area, were immersed in Jena flasks containing vigorously boiling solutions of common salt of various concentrations. The flasks were then sealed with tightly fitting rubber bungs, coated with paraffin wax, and set in an inverted position in beakers of water as shown in Fig. 41. In this it was easy to see if the flasks remained air-tight during the course of the experiments. After the lapse of seventeen days, one or two of the strips were slightly tarnished where they rested upon the rubber stopper. Elsewhere, however, they remained bright. On opening and weighing the metal, the results detailed in the following table were obtained:—

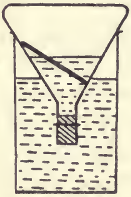
FIGURE 41.

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[1] Since the above was written Mr. Jos. H. Brown and the Author have observed that the explanation for this anomaly lies in the temperature at which the experiments were carried out. At 10° C. solutions of sodium chloride yield critical concentrations whose corrosive action upon iron is greater than that of distilled water at the same temperature. At 21° C. results almost identical with those of Heyn and Bauer were obtained. At 14° C. the critical concentration exerted *the same* corrosive action as distilled water; 14° C. may hence be termed the *Inversion Temperature.* These results are of peculiar interest as showing that, in the tropics, salt water is less corrosive than fresh water, whereas in more temperate climes the reverse may be the case, at any rate during the winter. Further experiments along these lines are in progress.

[2] Adie, "Min. Proc. Inst. Civil Engineers," 1845, 4, 323.

Weight of Salt in Grm. per Litre.	Weight of Iron Before Experiment. Grm.	Loss in Weight. Grm.	Remarks.
0·0	1·2838	0·0004	One corner, in contact with rubber, tarnished.
0·6	1·2952	0·0006	End in contact with rubber stained blue. Easily wiped off.
2·0	1·2488	0·0006	Slightly more attacked. Stain more difficult to remove.
6·0	1·2820	0·0004	Exceedingly slight superficial tarnish.
Saturated solution	1·1678	0·0002	Same.

Clearly, therefore, solutions of sodium chloride at the temperature of the room and in the absence of air exert no appreciable action upon iron. The tarnishing referred to in the above table was undoubtedly caused by the presence of traces of sulphur in the rubber bungs.

The influence exerted by nitrates upon the corrosion of iron is interesting inasmuch as rain water, particularly in thunderstorms, contains nitric acid, either free or combined, and this exerts a pronounced corroding action upon iron. Sewage also contains nitrates and nitrites in solution, and these salts find their way into purified sewage water which is used in feeding boilers, causing pitting and serious damage.[1] The results obtained by Friend and Brown for solutions of potassium nitrate are shown graphically in Figs. 39 and 40.

J. B. Senderens[2] has studied the action of nitrates upon iron wire, and the reader desirous of pursuing the subject further may be recommended to study his memoir. Owing to its presence in sea water, magnesium chloride has received a good deal of attention from chemists in respect to its corrosive action. In Fig. 42 the loss in weight of iron plates immersed in solutions of magnesium chloride, as determined by Heyn and Bauer, is shown graphically. In the absence of air this salt is capable of acting upon iron, particularly if the temperature is raised, and this property greatly enhances its corrosive power in air. Wagner,[1] appears to have been the first to call attention to this, and Dobbs[2] has emphasized the fact in connexion with its practical bearing upon engineering problems.

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[1] See W. Thomson, "J. Iron Steel Inst." 1894, I, 597; from "Trans. Manchester Assoc. Engineers," 1893, p. 245.

[2] Senderens, "Bull. Soc. Chim." 1897, 15, 691.

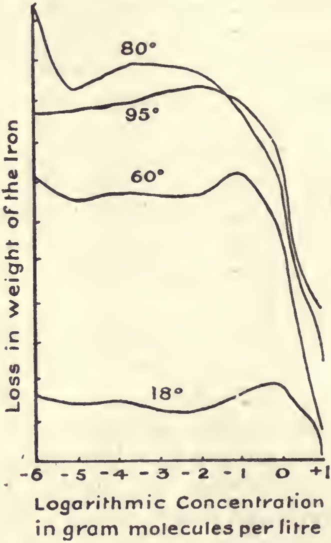

FIGURE 42.—CORROSIVE ACTION OF MAGNESIUM CHLORIDE SOLUTIONS.

The retarding action of arsenious oxide upon the corrosion of iron has been known for many years.[3] Burgess and Engle[4] have recently drawn attention to the interesting fact that traces of arsenious oxide greatly retard the vigour with which dilute sulphuric and hydrochloric acids attack metallic iron. The connexion between these two phenomena is obvious when we remember that corrosion is primarily the result of acid attack.

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[1] Wagner, "Dingler's Polytechn. J." 1875, **218**, 70.

[2] Dobbs, "Trans. N.E. Coast Inst. Engineers and Shipbuilders," **5**, pp. 196, 197, 247.

[3] Compare Lindet, "Compt. rend." 1904, **139**, 859.

[4] Burgess and Engle, "Trans. Amer. Electrochem. Soc." 1906, **9**, 199.

Heyn and Bauer[1] have carefully studied this subject and give the following details of their work and its result. Sections of a mild steel bar, measuring 2·3 × 2·3 × 0·6 cm., and having the composition given on p. 244, were first polished bright on an emery wheel and then suspended by means of a glass rod in a beaker containing 500 c.c. of 1 per cent sulphuric acid, to which varying quantities of arsenious acid were added. It was found that an addition of 0·0069 grm. of arsenious oxide, As_2O_3, reduced the attacking power to one-third. Further increase in the amount of oxide reduced the power of the acid still more, but with less rapidity, the curve approaching asymptotically towards a lower, limiting value. This is well shown by Fig. 43, in which the results are given graphically.

Heyn and Bauer have further demonstrated the fact that the presence of elementary arsenic in the vessel containing the attacking sulphuric acid exerts a like retarding effect, as does also the passage of arseniuretted hydrogen through the liquid.

Ammonium salts of mineral acids are remarkably corrosive, as is evident from a consideration of the curves in Fig. 44, in which the results of Heyn and Bauer are given. The nitrate is the worst offender, and this is a point of great importance in connexion with the corrosion of iron exposed to the direct action of rain and the atmosphere generally. In thunderstorms, as is well known, ammonium nitrate is invariably produced, which is dissolved by the rain on its downward path. Although the rain, falling under these conditions, is only an excessively dilute solution of ammonium nitrate, the concentration naturally increases as evaporation takes place until the critical value is approached, the rate of evaporation falling off rapidly as the concentration of the salt increases. It is easy to understand, therefore, why iron exposed to such action should suffer considerable corrosion in a comparatively short time.

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[1] Heyn and Bauer, "J. Iron Steel Inst." 1909, I, 109.

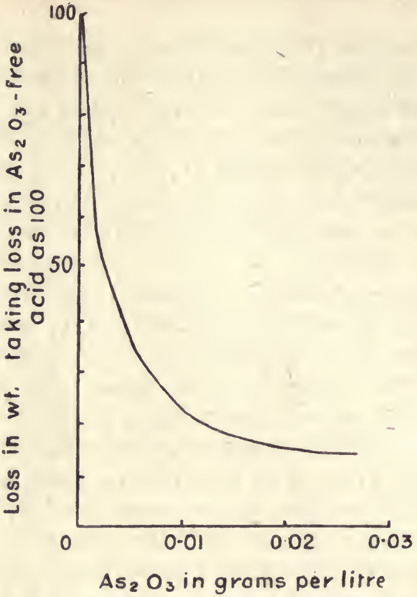

FIGURE 43.—CURVE SHOWING THE REDUCTION OF THE ATTACKING POWER OF SULPHURIC ACID BY THE PRESENCE OF ARSENIOUS OXIDE (HEYN AND BAUER).

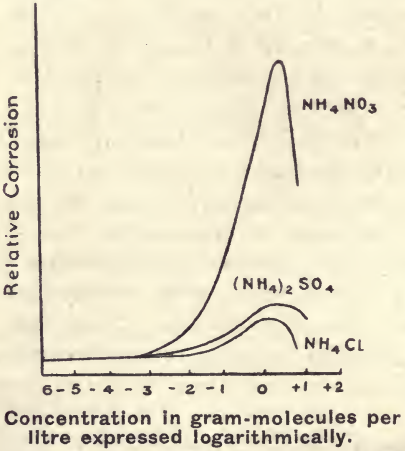

FIGURE 44.—CORROSION INDUCED BY SOLUTIONS OF AMMONIUM CHLORIDE, SULPHATE, AND NITRATE, ACCORDING TO HEYN AND BAUER.

Heyn and Bauer show that solutions of ammonium nitrate exert a corrosive action upon iron in the absence of air, practically equal in extent to that observed when air had free access to the liquid, both ferrous and ferric iron being found in solution after three weeks. Solutions of ammonium chloride and sulphate solutions acted similarly, but to a much less extent, the iron in solution being almost entirely in the ferrous condition. The numerical results obtained are given in the following table, and will serve to make these points clear.

THE ACTION OF CRITICAL SOLUTIONS OF AMMONIUM SALTS UPON IRON BOTH IN THE ABSENCE AND IN THE PRESENCE OF AIR (HEYN AND BAUER).

Salt.	Conc. of Salt in Grm. per Litre.	Loss in Weight of Iron in Presence of Air. A	Loss in Weight of Iron in Absence of Air. B	Ratio $\frac{B}{A} \times 100$
NH_4NO_3	500	1·6212	1·5006	92
$(NH_4)_2SO_4$	200	0·3418	0·0570	17
NH_4Cl	100	0·2451	0·0056	2·3

CONSIDERATION OF THE RESULTS.

The question which now arises is: What interpretation are we to put upon the remarkable results which we have just been considering? A fairly complete answer to this question, in so far as it applies to the passivifying reagents (chromic acid and its soluble salts) mentioned in Group I, will be found in Chapter XII, which is devoted entirely to a consideration of the phenomena of passivity. In the case of the other substances, however, we must look to another source.

Probably when iron is immersed in solutions of electrolytes, a portion of the metal passes into solution with the production of a ferrous salt. For example, if sodium chloride be the electrolyte in question, we may represent the condition of affairs by the equation :—

$$Fe + 2NaCl + 2H_2O \rightleftharpoons FeCl_2 + 2NaOH + H_2$$

the reaction proceeding in this particular case to a minute extent only upon the surface of the metal, which now becomes coated with a thin film of hydrogen.[1] If air be now admitted to the system, the free hydrogen is oxidized to water, the iron already in solution yielding ferric hydroxide, and more metal is dissolved to restore equilibrium, and corrosion proceeds apace. By increasing the concentration of the electrolyte, the equilibrium is pushed from left to right, so that an increased rate of corrosion is to be expected. This explains the ascendant portion of the curve CD in Fig. 30 (p. 131).

Opposed to this, however, we have the decreased solubility of the oxygen in the water as the concentration of the electrolyte increases, which means a reduction in the rate of corrosion; and the actual extent to which corrosion does proceed will thus be a measure of the relative strengths of these two opposing forces.

Since for dilute solutions of an electrolyte the solubility of the oxygen is but little affected, the rate of corrosion of the iron will at first tend to increase with the concentration. A maximum will ultimately be reached (D, Fig. 30), after which the corrosion will decrease, as the effect of the concentration of the electrolyte upon the oxygen solubility becomes marked.[2]

The extraordinary corrosive action exhibited by the ammonium salts receives a ready explanation from the fact that they are largely hydrolyzed in aqueous solution, and thus partake more of the nature of acids than of neutral salts.[1]

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[1] The author is aware that this view is not generally accepted by chemists; but in view of the recent work of Ipatieff and Werchowsky ("Ber." 1909, **42**, 2078), who have shown that metals may be precipitated out of their salts by subjecting them to high pressures of hydrogen gas at slightly raised temperatures, there seems to be no reasonable objection to the assumption that such reactions as the above now under discussion are reversible, equilibrium being attained when a few atoms, only, of iron have passed into solution.

[2] Adie ("Min. Proc. Inst. Civil Engineers," 1845, 4, 323), appears to have been the first to draw attention to the close connexion between the solubility of oxygen and the rate of corrosion of iron in various salt solutions.

THE INFLUENCE OF TEMPERATURE UPON THE CORROSIVE ACTIVITY OF AQUEOUS SOLUTIONS OF SINGLE ELECTROLYTES.

Unfortunately this aspect of the subject has not as yet been thoroughly investigated, although the importance of thoroughly understanding it can scarcely be overrated.

The action of hot or boiling solutions of ammonium salts, usually the chloride, upon iron in the form of foil, drillings, or filings, has received attention from a number of independent workers from time to time. Thus Santi[2] shows that iron drillings are readily attacked by a hot concentrated solution of ammonium chloride, hydrogen and ammonia being evolved, according to the equation:—

$$Fe + 2NH_4Cl = FeCl_2 + 2NH_3 + H_2$$

the ammonium chloride thus acting virtually as a free acid. The ferrous chloride now combines with excess of the ammonium salt yielding a complex having the formula $FeCl_2 . 2NH_4Cl$.

This activity of the ammonium salts is a matter of great importance in many manufacturing processes. Thus Kempson & Co.[3] find that the cast-iron pipes lying between the tar still and water level in their condensers are particularly liable to corrosion, and this they attribute to the presence of ammonium chloride. These observations are supported also by the experience of Davis Bros. of Manchester.[4]

Many years ago Wagner[5] drew attention to a somewhat similar reaction which takes place between solutions of magnesium chloride and metallic iron. He describes an experiment in which 2 grm. of the neutral salt were introduced into a strong tube, together with weighed pieces of iron. Boiling distilled water was now added and the tube sealed. After keeping at a temperature of 100° C. for six weeks, the tube was cooled and opened, a considerable quantity of gas—presumably hydrogen—escaping. The iron was now black in colour and had lost 0·39 per cent in weight. On filtering the liquid, ferrous chloride was found in solution.

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[1] See Nance, "Proc. Chem. Soc." 1906, **22**, 143.

[2] Santi, "Chem. Zentralb." 1904, II, 1625.

[3] See "J. Iron Steel Inst." 1908, I, 83.

[4] Davis, "J. Iron Steel Inst." 1908, I, 80.

[5] Wagner, "Dingler's Polytechn. J." 1875, **218**, 70.

These results are of interest inasmuch as magnesium chloride is found in considerable quantity in sea water, the corrosive action of which, upon the boilers of steamers, etc., was for a long time a source of serious trouble to the marine engineer.[1]

Cribb and Arnaud have studied the action of varying concentrations of sodium carbonate solution upon iron at 100° C., the duration of the experiment extending over twenty-four hours.[2] It is shown that the rate of corrosion under these conditions is much greater than is observed at the ordinary temperature of the room, as will be evident from a glance at Fig. 45, in which their results are shown graphically.[3]

It was desirable, however, that a series of experiments be tried at various temperatures, and not merely at 100° C. In an earlier chapter[4] we have already pointed out that raising the temperature of water containing iron plates introduces two opposing factors of corrosion. The direct effect of the rise in temperature is to increase the affinity of the oxygen for the iron and thus to stimulate oxidation. On the other hand, the solubility of the oxygen is simultaneously decreased, until at 100° C. it is nil, and corrosion cannot take place. It follows, therefore, that there must be some intermediate temperature at which the corrosive action reaches a maximum. This was found by Heyn and Bauer to be approximately 80° C. for distilled water alone, when the vessels were heated for a period of seven hours only per day. In the case of electrolytic solutions now under discussion, however, we have yet a third factor to consider, namely, the action of the electrolyte itself upon the iron. In some cases, as for example that of sodium chloride, this is practically nil for pure iron.[1] Magnesium and ammonium chlorides, on the other hand, readily effect the solution of the iron even in the absence of air, as we have already seen, and are thus capable of causing active corrosion. Salts, such as ammonium nitrate, which contain loosely combined oxygen of their own, can not only dissolve iron, but also effect complete oxidation in the entire absence of air. As the temperature is raised, therefore, the last-named salts are particularly corrosive, for the rate of chemical action is greatly accelerated, and, being practically independent for support

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[1] The reader may here be referred to the experiments of D. Phillips ("Min. Proc. Inst. Civil Engineers," 1886, **85**, 295), "On the Effect of various kinds of Liquids, Hot and Cold, on Iron". The method of experiment was, however, rough and ready, and the range covered far too large for so few experiments. Consequently it is difficult to draw any general conclusions from the work.

[2] Cribb and Arnaud, "Analyst," 1905, **30**, 225.

[3] See note, p. 118.

[4] See Chapter VI.

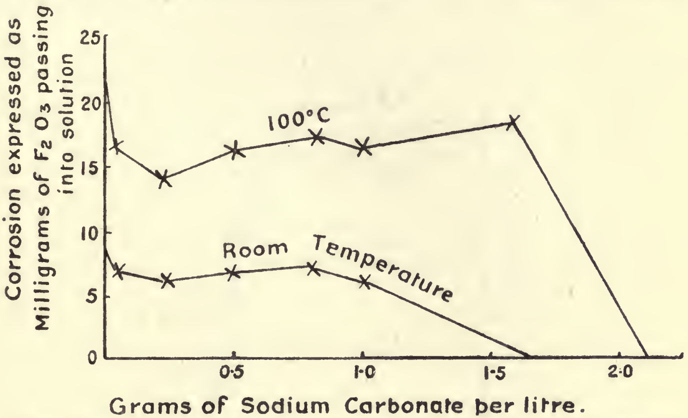

Figure 45.—Cribb and Arnaud's Results for the Corrosive Action of Sodium Carbonate Solutions at Room Temperature and at 100° C.

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[1] If the iron be impure, further complication arises owing to the induction of local galvanic activity, which leads to pitting—a most serious form of corrosion. This will be fully discussed in a later chapter.

upon the dissolved oxygen, there is thus no opposing factor to reduce the corrosion.

Clearly, therefore, each case will have to be considered upon its own individual merits, a fact which renders generalization difficult. Heyn and Bauer have carried out a few experiments with solutions of sodium chloride and of magnesium chloride. Plates of mild steel, the analysis and dimensions of which are given on p. 129, were suspended, as shown in Fig. 28, p. 128, in solutions of these electrolytes, and heated in a glycerine-bath maintained for seven hours each day at a certain temperature, this process being continued for twenty-two days. The results obtained are given graphically in Figs. 46 and 42 respectively. As the temperature rises from 18° to 40° C., the corrosion is well-nigh doubled. Here, then, we have an explanation for the oft-repeated observation that tropical sea waters attack our iron and steel-cased vessels with considerably greater vigour than do

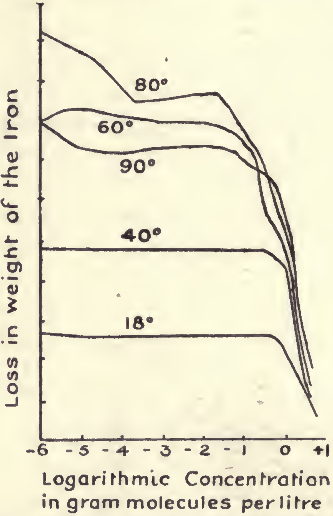

Figure 46.—The Action of Sodium Chloride Solutions upon Iron of Various Temperatures (Heyn and Bauer).

those of more temperate climes. At 80° C., in the case of the more dilute solutions, the corrosion reaches a maximum.

All these experiments, however, can at best be considered as merely of a preliminary nature, and further work on this subject is urgently needed.

X.

THE INFLUENCE OF AQUEOUS SOLUTIONS OF TWO OR MORE ELECTROLYTES UPON IRON.

It rarely happens in actual practice that iron is exposed to the action of single electrolytes only. The problem of corrosion is invariably far more complicated owing to the presence of several electrolytes, whose concentrations seldom remain constant. A thorough study of the action of mixtures of electrolytes must of course be preceded by that of the individual salts alone. This has already been accomplished to a certain extent, and a further continuation of the work along the lines laid down in this chapter is highly desirable.

Heyn and Bauer[1] have very recently given the result of a research into the action of mixtures of solutions of the chloride and carbonate of sodium upon iron at varying dilutions, the relative proportions of the salts being 2 : 1, 1 : 1, and 0·5 : 1, respectively. In every case a critical concentration was observed which had the same value as that of sodium carbonate alone, namely, 1 grm. of sodium carbonate per litre. Its corrosive action, however, was generally slightly greater. No limiting concentration was reached, the solution becoming saturated with one or other of the salts before complete protection of the metal could be obtained.[2] Friend[3] has made a thorough study of the influence exerted by mixtures of potassium chloride and hydroxide solutions upon pure iron at room temperature. Pieces of pure Kahlbaum's iron foil, measuring 5 × 4 cm. in area, were placed in hard glass beakers as shown in Fig. 29, p. 130, each beaker containing 100 c.c. of liquid and one piece of metal only, which latter had been carefully weighed. Six or eight such beakers constituted a series in which the strength of the potash solution remained constant throughout, the amount of potassium chloride present being the only variable factor. The experiments were carried out in the laboratory during the summer vacation when the atmosphere was very free from carbon dioxide and gaseous impurities generally. For twenty-eight days the vessels were allowed to remain undisturbed exposed to air and diffused daylight, being shielded from dust by large glass bell jars resting upon wooden blocks to admit of free passage of air. At the close of this period the iron plates were removed, cleaned, and weighed. The results obtained are given in brief in the following table, the figures in bold type indicating at a glance where corrosion has taken place.

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1910, **28**, 81.

[2] Wrought iron was used in these experiments, the analysis of which is given on p. 129.

[3] Carnegie Memoir, entitled "Corrosion and Preservation of Iron," "J. Iron Steel Inst." 1911.

ACTION OF MIXTURES OF POTASSIUM CHLORIDE AND HYDROXIDE UPON IRON.

KCl in Grm. per Litre.	Loss in Weight of the Iron with the Following Concentrations of KOH in Grm. per Litre.					
	0·0	2·8	11·2	28	56	168
0·0	**0·0685**	0·0000	0·0000	0·0001	0·0000	0·0001
5·0	**0·0884**	**0·0802**	0·0010	0·0008	0·0004	0·0000
15·0	**0·0836**	**0·0929**	**0·0074**	0·0002	0·0004	0·0000
50	**0·0828**	**0·0985**	**0·0354**	**0·0112**	0·0000	0·0001
150	**0·0790**	**0·0657**	**0·0334**	**0·0059**	0·0004	0·0003
300 (saturated)	**0·0390**	**0·0196**	**0·0104**	0·0010	0·0004	0·0002

In Fig. 47 the above results are shown graphically. In the absence of the caustic potash, corrosion proceeded uniformly, the surface of the metal being covered with a layer of brown rust which could easily be removed, showing the absence of any serious galvanic action. When potassium hydroxide was used, the corrosion was local in character, deep pits being formed in different places, the metal often being completely eaten through. The pits were frequently joined by a pretty tracery of fine threads of brown rust and dark green hydroxide.

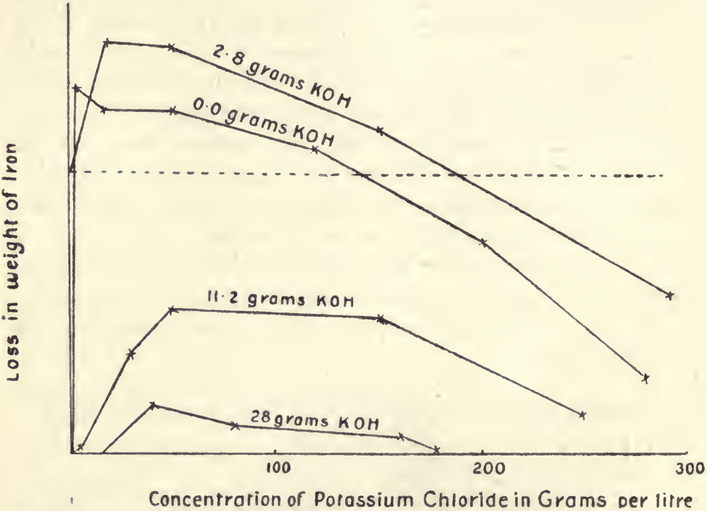

FIGURE 47.—THE ACTION OF MIXTURES OF KOH AND KCL UPON IRON (FRIEND).

All the curves agree, however, in showing critical concentrations, the corrosive action of which decreases as the amount of potassium hydroxide increases, becoming nil in the presence of 56 grm. of potash per litre.

These results may be represented in another manner in a series of curves (Fig. 48). AK represents the solubility curve of potassium chloride in solutions of the hydroxide, and CE the minimum concentrations of caustic potash required to completely prevent the corrosion of iron in the presence of corresponding amounts of potassium chloride. Within the area CEA, therefore, corrosion can readily take place, although the liquid is alkaline; but in BCEK, which may be called the inhibiting area, no rusting occurs.

This opens up to us at once a new aspect of the whole question, for it is generally assumed that, provided a small quantity of alkali is present, no corrosion of iron will take place. It will be clear that these results have a most important bearing upon the utility of cements, which consist essentially of an alkaline material, such as lime, in intimate association with corrosive electrolytes such as silicates, sulphates, etc., of magnesium, aluminium, and the alkaline earths. If such cements are to be reinforced with steel, it is essential that this latter metal be guarded from corrosion, otherwise nothing but disaster can follow in the wake.

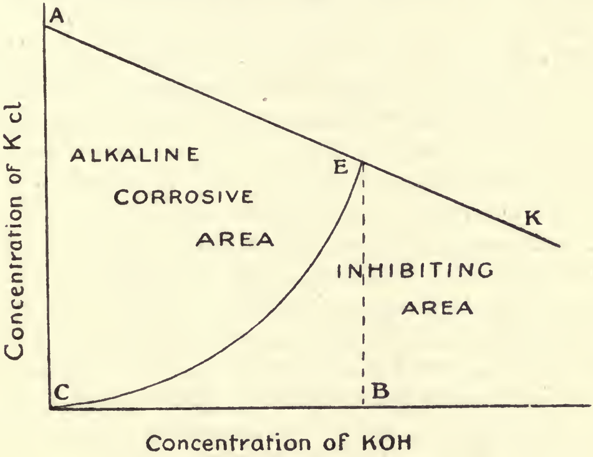

FIGURE 48.

Now, the preservation of the steel embedded in concrete depends upon two factors:—

1. The complete exclusion of air and moisture.
2. The inhibitive nature of the surrounding medium.

If the former of these factors could be absolutely relied upon, there would be less need to consider the second, for, in the absence of air or oxygen, a merely neutral or faintly alkaline cement would serve to protect the iron indefinitely. We must remember, however, that small bubbles of air are almost always shut in within the pores of the cement, and these may effect the corrosion of a very small portion of the iron. Furthermore, can we be certain that concrete is absolutely impervious to air and moisture when situated in damp places for years together? Probably not. In either case, if corrosion should take place to a small extent, the result may be serious out of all proportion. We have already seen that when iron corrodes it undergoes enormous expansion, a single unit of malleable iron yielding no fewer than ten of rust by volume[1] and the surrounding concrete must inevitably yield. A slight crack allows more air to enter, corrosion proceeds further, resulting in still greater expansion, and the consequences are clearly serious. If, however, the concrete have such an amount of free alkali present as is represented by any point well within the area BCEK, any small amount of air or moisture penetrating to the iron will have no effect whatever, and the structure may last indefinitely. Fortunately this is not a difficult matter, for the corrosive salts present in concrete are so slightly soluble in water, that a relatively small amount of free lime will suffice. But engineers must be careful to see that this minimum is added.

It must be remembered, however, that these remarks apply only to the most compact concrete, for if the latter be very porous—as it ought never to be—its free alkali will soon become neutralized, and corrosion must then proceed apace. An example of this has been given by Ford.[2] Here, then, we have an explanation for those terrible disasters which have resulted from the careless manner in which the ferroconcrete has been made.[3]

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[1] Bauermann, "J. Iron Steel Inst." 1888, II, 135.

[2] Ford, "Engineering News," 1905, **53**, 316.

[3] See Himmelwright, "Iron Age," 1907, **79**, 141; "Engineering News," 1906, **56**, 549.

When, however, the concrete is made compact, and thoroughly alkaline, the iron embedded within it will last for centuries, particularly if the iron bars be free from sharp corners, and have rounded edges to facilitate air escape and proper ramming of the concrete[1]. This is evident from a number of striking examples.

Two or three years ago a gasometer in Hamburg was pulled down after having been in use for half a century.[2] On removing the foundation piers by blasting, the iron anchor bolts of the superstructure were laid bare. Sixty of these were discovered, each 2 × 2 inches square and some 6 to 9 feet in length. They had been embedded in solid concrete which formed a covering $\frac{3}{4}$ inch in thickness, and appeared to have been run in round them at the time of placing in position in 1852. Not one of the pieces of metal showed signs of rust, but all exhibited the steel blue skin as fresh as on leaving the rolls.

Experiments carried out at our National Physical Laboratory upon mild steel embedded in Portland cement have given very encouraging results.[3] Although the cement was covered with water several times a week for a whole year, and for three months afterwards exposed to the open air and weathering, no trace of rusting or deterioration of the metal could be detected.

Numerous other examples[4] might be quoted, but the above are sufficient for our purpose.

It is interesting to note that the metal, before being embedded in the concrete, need not be cleaned from rust,[5] which is always a lengthy and tedious process. The alkali in the cement appears to dissolve the oxide with the formation of alkaline ferrites or ferrates, leaving the surface of the metal clean and bright.[1]

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[1] E. Noaillon, "J. Iron Steel Inst." 1905, II, 740; from a paper read before the Mech. Eng. Inst., June, 1905.

[2] Zement und Beton, 1908, No. 48. Zeit. oesterr. Ingenieur und Architekten Vereines, **61,** 175.

[3] Glazebrook, "Times Engineering Supplement," 20 May, 1908.

[4] See "Engineer," **107,** 628. "Iron Age," 1903, **72,** 43. H. C. Turner, "Engineering News," 1904, **52,** 75; 1908, **59,** 153. Dunn, "J. Roy. Inst. British Architects," **12,** 21. Norton, "Engineering News," 1904, **51,** 29; 1902, **48,** 333. Thwaite, "Iron and Steel Magazine," 1906, **11,** 411. Turner Construction Co., "Engineering News," 1904, **52,** 153.

[5] Blount, "Trans. Inst. Civil Engineers' Conference," § 4, pp. 110, 1907.

But we must guard against the error of over-confidence in reinforced concrete, even if perfectly manufactured, imagining that it will stand any and every kind of treatment, without suffering appreciable deterioration. The fallacy of such an assumption has been emphasized by Knudson,[2] and Toch,[3] who point out that no matter how perfect the cement, corrosion of the iron will certainly take place if subjected to the action of electric currents.

This is a point of very great importance, and must be reckoned with in the construction of all new buildings. U. J. Nicholas[4] has thoroughly investigated the question and finds that, in such circumstances, even neat cement itself can afford no protection to the iron. He further shows that a continuous current of only 0·1 amperes is sufficient to produce disastrous results.[5]

These are undoubted facts, and deserve the most serious consideration from all whom they may concern.[6]

[1] Rohland, "Stahl und Esien," 1909, **29**, 408; 1907, **27**, 156. Mouchell, "J. Roy. Inst. British Architects," **12**, 47. Compare also, "Report of Boston Transit Committee," 1904, **10**, Appendix F2, p. 81. Schaub, "Engineering News," 1904, **51**, 561. F. W. Taylor and S. E. Thompson, "Treatise on Concrete, Plain and Reinforced," 1905.

[2] Knudson, "Trans. Amer. Inst. Electrical Engineers," 1907, **26**, Part I, p. 231. See "Electrician," 1907, **59**, 213.

[3] Toch, "Proc. Amer. Soc. Testing Materials," 1906, **6**, 150; "Trans. Amer. Electrochem. Soc." 1906, **9**, 77.

[4] Nicholas, "Engineering News," 1908, **60**, 710.

[5] See Chapter XIV.

[6] The reader, interested in this part of our subject, is referred to the following literature, in addition to that already quoted: Breuille, "Annales des ponts et chaussées, mémoires," ser. 8, Vol. III, 1er trimestre, 181 (1902.) Buel, "Engineering Record," 1898, **38**, 278, 409. W. H. Fox, "Engineering News," 1907, **57**, 569. Hinrichsen, "Mitteilungen aus dem königlichen Material-prüfungsamt," 1907, **25**, 321. Langsdorf, "J. Assoc. Engineering Societies," 1909, **42**, 69. Lidy, "Annales des ponts et chaussées, mémoires," ser. 7, Vol. XVIII, 4e, trimestre, p. 229 (1899). Lindeck,

Friend and Brown[1] have studied in detail the action of mixtures of potassium bichromate and sodium chloride solutions upon iron, in a similar manner. Their results are given graphically in Fig. 49, and are of particular interest for the following reasons.

For many years chemists have been familiar with the fact that iron may be kept for an indefinite time in contact with solutions of potassium bichromate (unless these are excessively dilute) without undergoing any visible change in appearance. This is usually attributed to the formation, upon the surface of the iron, of a layer of oxide of such tenuity as readily to escape observation, which layer protects the underlying metal from attack—a phenomenon generally known as *passivity*.[2] Cushman[3] has made this the subject of special study, and suggests that the addition of approximately five[4] pounds of potassium bichromate to every 1500 gallons of water (equivalent to 0·36 grm. per litre) should prove very useful as a protection against excessive boiler corrosion; for, with such a concentration, samples of steel and iron were observed to remain free from rust in the boiling solutions for an indefinite period, although air was continually bubbled through.

"Elektrotechnische Zeitsch." 1896, **17**, 180. Matthews, "Iron, Coal Trades' Review," 1909, **78**, 544. Spencer Newberry, "Engineering News," 1902, **47**, 335. Norton, "Iron Age," 1902, **70**, 7. Rohland, "Ton-industrie Zeitung." 1908, **32**, Part II, p. 2049, also 1909, **33**, 283. Toch, "J. Amer. Chem. Soc." 1903, **25**, 761. Wagoner and Skinner, "Engineering News," 1906, **56**, 458. Whiskeman, "Engineering Record," 1903, **47**, 394. Thwaite, "Concrete and Constructional Engineering," **1**, 46-50.

[1] Paper entitled "The Action of Aqueous Solutions of Single and Mixed Electrolytes upon Iron," read May 11, 1911, before the Iron and Steel Institute, London.

[2] See Chapter XII, where the subject of Passivity is fully discussed.

[3] Cushman, U.S. Department of Agriculture, 1907, Bulletin No. 30.

[4] Cushman states that $\frac{1}{100}$ normal bichromate is the necessary minimum concentration to protect iron from corrosion at the boiling temperature of water, and that this is equivalent to approximately *one* pound of the bichromate in 1500 gallons. This latter statement, however, is clearly a misprint for *five* pounds.

The suggestion, however, is based on the assumption that the feed water for the boilers is pure—a condition of affairs which rarely obtains in practice; and one is naturally led to ask what effect the presence of varying quantities of foreign substances might have. For example, if a little sodium chloride

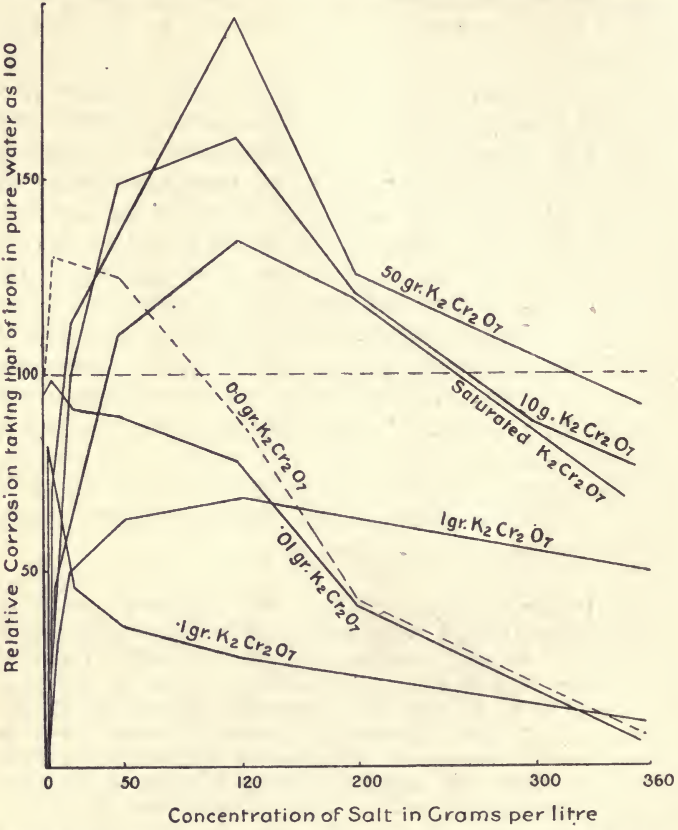

FIGURE 49.—SHOWING THE ACTION OF MIXTURES OF POTASSIUM BICHROMATE AND SODIUM CHLORIDE SOLUTIONS AT ROOM TEMPERATURE UPON IRON (FRIEND AND BROWN).

be added to a solution of bichromate, interaction will take place between the two salts until an equilibrium is established, as indicated by the equation :—

$$H_2O + K_2Cr_2O_7 + 2NaCl \rightleftarrows K_2CrO_4 + Na_2CrO_4 + 2HCl.$$

The free hydrochloric acid thus liberated may now be expected to dissolve the protective film of oxide on the iron, and thereby expose a fresh surface of metal to attack, with the result that corrosion proceeds apace. This has already been proved to be the case in a series of qualitative experiments.[1] The problem is interesting, for we thus have two opposing factors to consider, namely :—

1. The protective action of the bichromate, and
2. The corrosive action of the acid,

from which it follows that the actual corrosivity observed must be the resultant of these forces.

In order to obtain a quantitative idea of this, several series of experiments were carried out at the ordinary temperature of the air in the manner already indicated, each series containing a definite and fixed quantity of potassium bichromate in solution, with varying amounts of sodium chloride. The results are shown graphically in Fig. 49. We see that when the concentration of the bichromate does not exceed 0·01 grm. per litre, its protective action is relatively slight. The best results are yielded with 0·1 grm. of bichromate, unless the concentration of the sodium chloride is small, namely, appreciably less than 5 grm. per litre, in which case a stronger solution, namely one containing 1 grm. of bichromate per litre yields better results. Further increase in the concentration stimulated the corrosion, a maximum being reached with a 5 per cent solution, the action being far greater than that manifested by pure sodium chloride alone.

Nor is the explanation far to seek. By increasing the concentration of the bichromate we disturb the equilibrium indicated by the equation given above, causing the reaction to proceed to a greater extent from left to right, and thus increase the amount of free acid in solution, thereby accelerating the corrosion of the metal.

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[1] Friend, "J. Iron Steel Inst." 1908, II, 9.

The practical importance of these results is clear. For tanks kept at ordinary temperatures and holding liquids containing appreciable quantities of salts (not necessarily common salt, of course, for the same kind of reaction will take place if practically any other salt be present), an addition of 0·1 grm. of potassium bichromate per litre of water, equivalent to 1 lb. of bichromate per 1000 gallons, will exert a marked retarding action upon corrosion. If the concentration of the dissolved salts is small, namely appreciably less than 5 grm. per litre, or 50 lb. per 1000 gallons, that of the bichromate may with advantage be increased to 1 grm. per litre or 10 lb. per 1000 gallons. As we shall presently see, however, much better results can be obtained in another manner.

The above results do not apply to boiling solutions such as one has to treat of in boilers. A series of experiments was carried out in which the solutions containing the iron were maintained at approximately 95° C. for twelve hours per day for three days by standing in a specially constructed hot-water bath. At night-time the bath was allowed to cool down to the temperature of the laboratory. The results are shown graphically in Fig. 50.

As before, the presence of 0·1 grm. of bichromate per litre exerts a powerful retarding action upon the corrosion of the metal, and is clearly the best concentration to employ. 1·0 grm. of bichromate is far less beneficial, and in the presence of small quantities of sodium chloride, considerably enhances the corrosive action of the liquid. Herein, therefore, lies the great objection to the use of bichromate, for, in the majority of cases in practical life, it would be impossible to regulate the concentration of the salt to such a nicety as to obtain the maximum efficiency.

It is noteworthy that by greatly increasing the concentration of the bichromate the extent of the corrosion is not proportionately severe, as was found to be the case at ordinary temperatures. Evidently the increased protective oxidizing power of the bichromate induced by rise of temperature counterbalances very effectively the increased corrosive effects of the liberated acid.

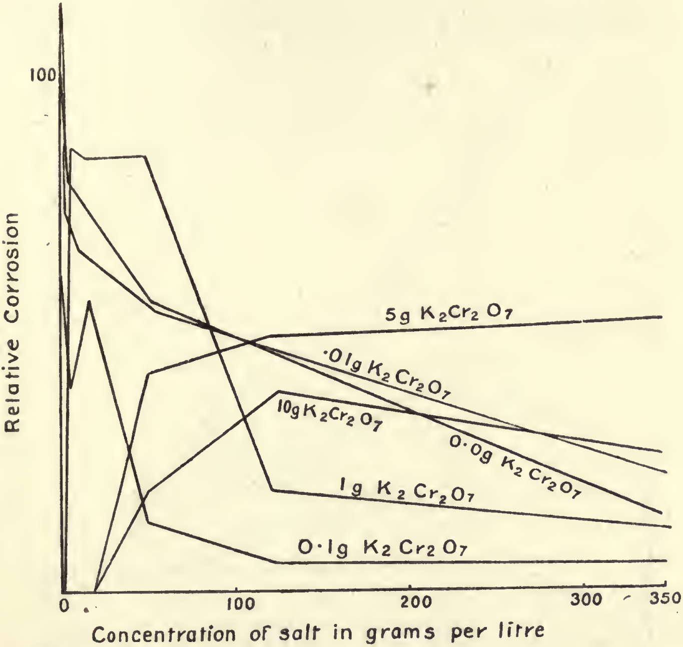

Figure 50.—Showing the Action of Mixtures of Potassium Bichromate and Sodium Chloride Solutions Upon Iron at 95° C. (Friend and Brown).

Considerably better results are to be expected if a chromate is used instead of a bichromate, for no free acid will be generated by the addition of foreign salts. For example, on the addition of sodium chloride to a solution of potassium chromate, the equilibrium ultimately arrived at may be represented by the equation :—

$$2NaCl + K_2CrO_4 \rightleftarrows Na_2CrO_4 + 2KCl.$$

This is obviously equivalent to adding an alkali to the mixture of bichromate and sodium chloride, and we now have the same

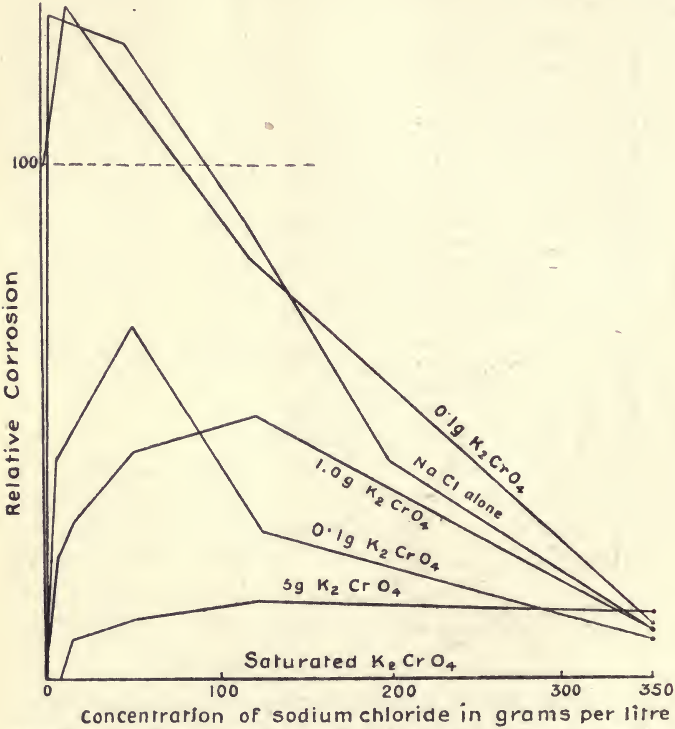

FIGURE 51.—SHOWING THE ACTION OF MIXTURES OF POTASSIUM CHROMATE AND SODIUM CHLORIDE SOLUTIONS UPON IRON AT ROOM TEMPERATURE (FRIEND AND BROWN.)

passivifying or oxidizing force, tending to inhibit corrosion, as before, and we have in addition reduced the corrosive force of the free acid by neutralization. That such a procedure is far more effective in reducing corrosion is evident from the results of Friend and Brown, shown graphically in Fig. 51, which were obtained in a precisely similar manner to those given in Fig. 49.

One great advantage lies in the fact that too much chromate cannot be added since, by increasing its concentration even up to saturation, no ill effects are produced, but the tendency to corrode is reduced still more. Similar remarks apply to the efficiency of the chromate solutions at boiling temperatures, as a glance at Fig. 52 will show. These results were obtained in a similar manner to those given in Fig. 50. Clearly the addition of 1 grm. of potassium chromate per litre, corresponding to 10 lb. of the salt per 1000 gallons of water, exerts a marked retarding effect upon corrosion. A further increase in concentration of chromate is more beneficial in the presence of small amounts of sodium chloride, an excellent protection being secured with 100 lb. per 1000 gallons (10 grm. per litre).

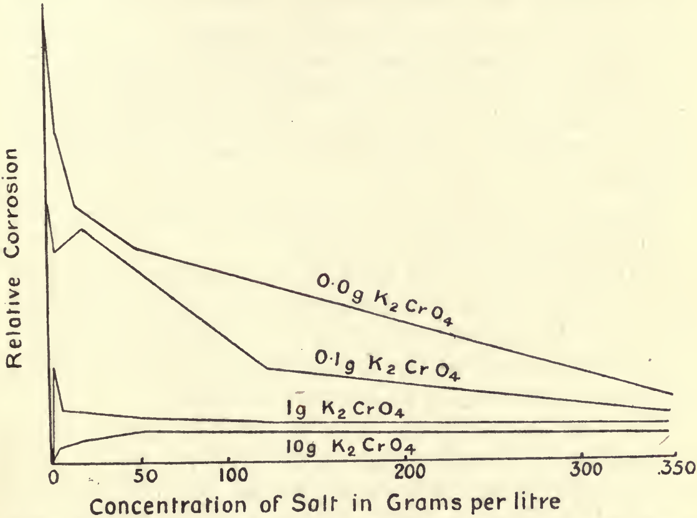

FIGURE 52.—SHOWING THE ACTION OF MIXTURES OF POTASSIUM CHROMATE AND SODIUM CHLORIDE SOLUTIONS UPON IRON AT 95° C. (FRIEND AND BROWN.)

These results are worthy of careful consideration by practical men.

THE ACTION OF SEA WATER UPON IRON.

That sea water is a particularly corrosive liquid has been a matter of common knowledge for many years. Thus, as early as 1845, Adie[1] showed by quantitative experiments that iron was more vigorously attacked by sea water in the presence of air, than by fresh water under like conditions. He found, for example, that twenty pieces of wrought iron wire immersed in sea water for eighty days lost 2·6 grains in weight, whereas in fresh water the loss amounted to only three quarters of this, namely 1·9 grains. Cast iron was shown to be similarly affected.

The activity of sea water is traceable to a variety of causes, which may be enumerated as follows:—

1. Owing to tidal forces and to winds generally which constantly stir up the waters, oft-times in the form of fine spray, the sea always contains a large quantity of dissolved oxygen—a condition of affairs which we have already seen in an earlier chapter to be particularly favourable to corrosion.

That this cannot be the only cause of the activity of sea water, however, is evident from the following two facts:—

(*a*) Oxygen is actually *less* soluble in sea water than in fresh water, as Adie very definitely proved, and later investigators have subsequently confirmed.

(*b*) Iron is attacked by sea water even in the complete absence of air, a fact which Payen[2] appears to have been the first to establish. On the other hand, iron may be kept for an indefinite time in fresh water which has been freed from dissolved air by thorough boiling.

Evidently, therefore, we must seek for other causes of the extreme corrosivity of sea water; and this is not difficult.

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[1] Adie, "Min. Proc. Inst. Civil Engineers," 1845, **4**, 323.

[2] Payen, "Compt. rend." February, 1837, No. VI.

2. Sea water contains relatively large quantities of dissolved salts, the chief of which are sodium chloride, magnesium chloride and magnesium sulphate. As we saw in the previous chapter, each of these salts is capable of independently exerting a marked corrosive action upon iron, and in particular the magnesium chloride is vigorous in its attack owing to the fact that the absence of air does not prevent it, save to a relatively small extent. Herein, therefore, lies the secret of the activity of sea water.

When iron, whether wrought or cast, is exposed for long periods of time to the continuous action of sea water, more or less in the complete absence of air, as, for example, at considerable depths below the surface of the sea, it undergoes slow oxidation to ferrous oxide, becoming extremely soft, although at the same time it retains its original shape. The carbon content of the metal is usually thrown out as a graphitic mass, throughout the pores of which the ferrous oxide is lodged. The specific gravity is invariably reduced. Mallet[1] stated that he had in his possession a sample taken from the cast-iron keel of a ship which had been completely altered by exposure to sea water, its specific gravity being 1·259, whereas the average for cast iron is 6·8 to 7·6, according to the particular grade. During this change some of the iron is undoubtedly lost as ferrous chloride, $FeCl_2$, due to double decomposition with the magnesium chloride, and this, being soluble in water, is washed away. This assumption is rendered very probable by Hatchet,[2] who analysed a piece of altered metal and found it to contain :—

FeO	81 per cent
Graphite	16 ,,
Iron chloride	trace

The remainder being presumably silica and other insoluble materials which may have been originally present in the metal.

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[1] Mallet, "British Association Reports," 1837.

[2] Hatchet, quoted by Mallet, *ibid.* 1837.

The changed metal is generally so soft as to be readily cut with a knife, and, upon exposure to the free air, not infrequently oxidizes to the ferric condition with such vigour as to considerably raise the temperature of the whole mass. According to Mallet, however, such is not *always* the case.

The classical instance in the case of cast-iron is that quoted by the great Swedish Chemist, Berzelius,[1] of the cannon balls raised at Karlskrona from a ship which had been sunk for fifty years. The metal had been entirely converted into a porous, graphitic mass, which spontaneously heated on exposure to air for fifteen minutes.

Rennie[2] instances the case of cast-iron guns fished up in 1822 off Holyhead. It appears that they had belonged to some pirate vessel destroyed some hundred years previously. When brought out of the water they were quite soft, but on exposure to the air they hardened to such an extent that they were used to fire salutes when King George IV passed through Holyhead on his way to Dublin a little later. It was observed that these old guns gave louder reports than any others.

More recently Lidy[3] has described some objects dredged up in the harbour at Brest. These consisted mainly of cannon balls and shells dating from 1652 to 1791. They were covered with a hard coating several inches in thickness, composed of sulphides, sand, rust, and calcareous matter. The iron within could readily be cut with a knife, when it exhibited a black section similar to graphite, but one which readily tarnished. Analysis showed that the metal had originally been cast iron. Some articles, which had evidently been wrought iron, were similarly affected, whereas others had been attacked in a somewhat different manner.

About the same time Le Naour[4] examined some cannon balls which had lain in the sea for some one hundred to one hundred and fifty years. At first sight they appeared to have suffered but little change. Further examination showed, however, that not only was their specific gravity greatly reduced, but their cohesion, hardness, and toughness were almost completely lost. Exposure to the air caused a rapid rise in temperature, and a thermometer bulb pushed into 80 grm. of the powdered mass rapidly indicated a rise of temperature from 15° C. to 85° C. Under the microscope the texture was seen to be porous, and analysis subsequently showed that a considerable quantity of iron had disappeared, the proportion of carbon being rendered thereby abnormally high.

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[1] Berzelius, Traité de Chimie, 1831, Vol. III.

[2] Rennie, "Min. Proc. Inst. Civil Engineers," 1845, **4**, 323, who took part in the discussion of Adie's paper.

[3] Lidy, "Engineering News," 1897, **39**, 85.

[4] Le Naour, "J. Iron Steel Inst." 1898, I, 526; from "Génie," **31**, 271.

Mention should here be made also of Draper's[1] interesting account of a piece of altered grey cast iron which had come into his possession. The metal had formed part of a rail in the port of Dublin, and for twenty-five years had lain at about half tide level. It may therefore be assumed that for a total period of twelve and a half years it had been immersed in the sea water, and for a like period exposed in a more or less dry condition to the free atmosphere. The fragment weighed 557·31 grm. and measured 85 × 52 × 20 mm. Its lateral surface bore a slight incrustation of ferric oxide, but its upper surface had been converted for a depth of some 7 mm. into a brownish grey graphitic mass, which could easily be removed with a knife, laying bare the bright surface of metallic iron beneath. The quantity of altered cast iron thus removed weighed nearly 68 grm., and was wholly attracted by a magnet. On treatment with dilute hydrochloric acid, hydrogen gas was evolved, ferrous chloride passing into solution, and leaving an insoluble residue of graphite. Some unaltered metal, therefore, was present in the changed mass, possibly as carbide.

The above accounts refer in the main to cast iron, although Lidy mentions the case of a few wrought-iron articles which had undergone a similar change (*vide supra*) after prolonged immersion in Brest harbour. The earliest record, however, of wrought iron having been altered by sea water is probably that by Mallet,[1] who describes a portion of an ancient iron anchor which had come into his possession. The anchor had been taken up in Liverpool harbour, having been converted into a plumbago like mass, of unusual hardness and brilliancy, to the depth of half an inch. The iron which remained was remarkably pure. The specific gravity of the altered portion was 1·773 (pure iron has a specific gravity of approximately 7·8), and no particular heating effect was observed on exposing the mass to the air.

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[1] Draper, "Chem. News," 1887, **56**, 251.

A few other similar cases are on record, chiefly referring to cast iron, but the above contain all the essential phenomena that have been observed, and will therefore suffice for our purpose.[2]

THE ACTION OF GREASY WATER UPON IRON.

That grease is a remarkable preventative for corrosion has been known for many years, and the reason is not far to seek. Being in a high degree impervious to water, it prevents that liquid from coming into direct contact with the metal and thus removes one of the essential factors to corrosion. The case is otherwise, however, when small quantities of grease are present in the form of an emulsion in relatively large amounts of water. The majority of greases and oils in common use (save good lubricating oils of the paraffin series) are really organic salts, and consist of the base, glycerine, in combination with an organic acid. To take a concrete example, olive oil is essentially composed of glyceryl oleate, that is, the glycerine salt of oleic acid. Now, although these oils can be kept for a good while in contact with air and water at the ordinary temperature without undergoing any appreciable change, this is not the case if the water is heated, as in the case of boilers, etc. The oil now becomes decomposed into its two or more constituents—in other words, it is said to be hydrolyzed. Thus, for example, olive oil yields glycerine and oleic acid, according to the equation :—

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[1] Mallet, "British Association Reports," 1837, p. 259.

[2] The reader, wishing to become acquainted with the most important researches, in addition to those quoted above, dealing with the corrosive action of sea water, will find the following references useful: Hay, "Trans. Inst. Naval Architects," 1863, **4**, 149 Cowper Coles, *ibid.* 1866, **7**, 155. B. Bell, *ibid.* 1869, **10**, 174. Grantham, *ibid.* 1869, **10**, 174. T. Andrews, "Min. Proc. Inst. Civil Engineers," 1885, **82**, 281. King, "Trans. Amer. Soc. Mech. Engineers," 1894, **15**, 961. W. Thomson, "J. Soc. Chem. Ind." 1894, **13**, 118. Sabin, "Trans. Amer. Soc. Civil Engineers," 1896, **36**, 483; 1899, **43**, 444. Post, "Engineering News," 1901, **46**, 304. G. Johnstone, "Trans. Inst. Engineers and Shipbuilders," Scotland, 1901, **45**, 71. Cohen, "Trans. Inst. Naval Architects," 1902, **44**, 215. Rhoades, "J Amer. Soc. Naval Engineers," 1907, **19**, 379. Sherman, "Engineering News," 1909, **61**, 292. Kröhnke, "Metallurgie," 1910, **7**, 674.

$$\text{glyceryl oleate} + \text{water} = \text{glycerine} + \text{oleic acid},$$

which is closely analogous to the hydrolysis which we found ammonium salts to undergo when dissolved in water.

Now although pure glycerine itself has apparently no corrosive action upon iron[1] it cannot protect that metal in the presence of equivalent amounts of acid. The organic acid therefore attacks the iron with the formation of an organic salt, which is readily decomposed on admission of air, with the production of rust, the free acid being again liberated and thus rendered capable of attacking more iron. A small amount of grease, therefore, may be the means of doing an incalculable amount of harm, a fact which, as we shall presently see, has frequently been proved to be true in practice.

In the preparation of acid greases on a manufacturing scale, by boiling neutral fats with water, great difficulties are in consequence encountered, as we might expect.[2]

Owing to the fact that oils and greases are largely used as lubricants for machinery, and are thus liable to find their way into the feed water of boilers, the practical bearing of these points is too important to be overlooked. Stingl[1] appears to have been one of the first to draw attention to this. He instances the case of a gasometer whose cistern had been luted with greasy condensation water. In ordinary circumstances it should have withstood corrosive agencies for twenty or thirty years, but after four years the parts exposed to the greasy water were found to be eaten through. Mention is also made of two steam boilers which began to leak after only three weeks' firing, and had to be stopped and repaired a little later. The water had an opalescent appearance, due to presence of grease, as was evidenced by the fact of its complete removal on shaking with ether. Analysis showed the water to contain :—

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[1] Klein and Berg, "Compt. rend." 1886, **106**, 1170.

[2] See Cowper, "J. Iron Steel Inst." 1877, I, 131.

	In 10,000 Parts.
Calcium carbonate	1·3091 parts
Magnesium carbonate	0·6930 ,,
Calcium sulphate	0·3158 ,,
Magnesium chloride	0·0134 ,,
Sodium chloride	0·1200 ,,
Ferric oxide and alumina . . .	0·0241 ,,
Silica	0·0023 ,,
Organic matter	0·4138 ,,
Total	2·8915 ,,

The deposit from this water inside the boilers was greyish brown in colour, and of a friable nature. On addition of hydrochloric acid, effervescence was observed and a black, fatty mass floated to the surface.

In order to purify the water, chalk and part of the magnesium carbonate were precipitated, presumably by the addition of lime, and, on filtering, no grease could be detected in the filtrate, the fat particles in suspension having been completely carried down along with the insoluble precipitate. After repair the boilers were fed with this water and were then found to give every satisfaction. To purify such waters for high-pressure boilers, a mixture of lime water and caustic soda solution is recommended, as this serves the double purpose of removing the fatty acids and magnesia, which latter is objectionable in that it forms with the calcium sulphate at high temperatures very hard incrustations.

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[1] Stingl, quoted by Rowan, " British Association Reports," 1876.

It appears that, in the early days of railways on the Continent,[1] the engines which had undergone repair at the Frankfurt shops were observed to corrode very rapidly, whereas those repaired at Cologne did not. The cause was ultimately traced down to the fact that, at Cologne, the engines before leaving the sheds were washed out with soda, which removed all traces of grease. At Frankfurt this was not the case, and orders were at once given for it to be done, with the result that the trouble immediately ceased.

Numerous other cases might be quoted, but these are sufficient to show how essential it is that both the boilers themselves and the feed water should be free from grease. This means, of course, that the water-supply must be kept under strict analytical control. The danger incurred by lubricating oils finding their way into the tubes and boilers may be practically entirely overcome by using non-fatty oils only as lubricants; that is to say pure paraffin oils which can be obtained of all grades of consistency. As these contain carbon and hydrogen only they are unaffected by water at all temperatures and cannot, therefore, stimulate the corrosion of iron.

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[1] See "Stahl und Eisen," 1900, **20,** 263.

XI.

THE ACTION OF OILS UPON IRON.

THIN films of oil or fat spread over the surface of iron articles are well known to prevent corrosion of the metal during periods of idleness, and are consequently largely used. Furthermore, the so-called "lubricating" or "machine" oils are in enormous demand for reducing the friction in modern machinery; and many thousands of tons of the drying oils are annually applied to iron and steel structures throughout the civilized world, in the form of paints, lacquers, and enamels. It is highly desirable, therefore, that a careful study be made of the action of these oils upon iron for many reasons. Unfortunately, however, the subject has received but little attention from either chemists or engineers, and the remarks contained in this chapter must necessarily be few and somewhat disconnected.

1. THE DRYING OILS.

Since these oils are largely used in the manufacture of paint for iron work it is important to learn whether or not they are capable of dissolving iron to any appreciable extent. If they are, the coats of paint are liable to become saturated solutions of iron or of iron compounds, and, on exposure to moist air, will absorb water and oxygen with the formation of rust. Owing to the great increase in volume which this change brings about (see p. 158), the paint film may suffer partial disintegration. At the best it will be rendered porous and thus serve as a poor protection for the underlying metal. Other things being equal, therefore, the best drying oil for the manufacture of paint destined to be employed in the protection of iron work will be the one which exerts the least solvent action upon iron.

Marcy[1] exposed nearly 3 grm. of iron to the action of linseed oil at room temperature for ten days and found no loss in weight.[2] Evidently, therefore, linseed oil can have no very appreciable action upon iron.

Friend[3] has made a more searching test as to the action of several of the commoner drying oils upon iron. The oils were examined and found to be very pure, being perfectly neutral,[4] yielding normal specific gravities, saponification numbers and iodine equivalents. Pieces of Kahlbaum's pure iron foil, measuring 6 × 0·5 cm. in area, were sealed in glass tubes containing from 10 to 12 c.c. of oil, which half filled them, the remaining portion being occupied by air. One set of these tubes (A) was alternately heated to 100° C. during the daytime, and allowed to cool at night. After twelve days, during which the tubes had been maintained at 100° C., in all for about forty-five hours, the tubes were opened, the appearance of the metal noted, and any loss in weight determined. The results are given in the following table:—

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[1] Marcy, "Engineering News," 1893, **30**, 78.

[2] W. H. Watson ("British Association Reports," 1880; abstracted in "J. Iron Steel Inst." 1880, II, 665) found that linseed oil attacked iron with marked vigour in twenty-four hours, but as his results are abnormally high for all the oils he used, it is very probable that the latter were impure. We shall not, therefore, refer to these results again.

[3] Carnegie Memoir, entitled, "The Corrosion and Preservation of Iron," J. Iron and Steel Institute, London, 1911.

[4] This is a very important point, for many of the oils are refined by treatment with dilute sulphuric acid, and if this be not thoroughly washed out in later processes before the oil is placed on the market, one can readily understand that such oils would exert a most pronounced corrosive action upon iron, and indeed upon metals generally.

A. RESULT OF ALTERNATELY HEATING IRON TO 100° C. AND COOLING, FOR A PERIOD OF TWELVE DAYS.

Oil.	Initial Weight of Iron. Grm.	Loss in Weight. Grm.	Remarks.
Linseed (raw)	0·5384	0·0000	Metal bright.
Linseed (boiled)	0·5398	0·0002	Metal dull, slaty colour.
Poppy	0·5274	0·0000	Metal bright.
Tung (Chinese wood oil)	0·5392	0·0000	Metal bright.

Clearly, therefore, the solvent action of the oils upon iron is negligible under the above conditions, and as far as the metal is concerned there is no reason why, in cold weather, the paint to be applied to iron should not be first of all warmed, as has been frequently suggested. A second series of tubes containing larger pieces of iron foil, measuring 5 × 3 cm. in area, was kept for ten weeks at the temperature of the room with the following results :—

B. THE RESULT OF EXPOSING IRON TO THE ACTION OF OIL FOR TEN WEEKS.

Oil.	Initial Weight of Iron. Grm.	Loss in Weight. Grm.	Remarks.
Linseed (raw)	2·0866	0·0026	Metal bright.
Linseed (boiled)	2·0468	0·0000	Metal dull. Probably any slight loss through solution counterbalanced by increase through oxidation.
Poppy	2·0268	0·0050	Metal bright.
Tung	2·0974	0·0000	Metal bright.

A third series of experiments was carried out in a precisely similar manner to series B, but the metals were not weighed until after the lapse of five months.

C. THE RESULT OF EXPOSING IRON TO THE ACTION OF OIL FOR FIVE MONTHS.

Oil.	Initial Weight of Iron. Grm.	Loss or Gain in Weight. Grm.	Remarks.
Linseed (raw)	2·0504	−0·0005	Metal bright.
Linseed (boiled)	2·0796	+0·0022	Metal dull. Gain in weight due to oxidation.
Poppy	2·0526	−0·0006	Metal bright.
Tung	2·0388	−0·0004	Metal bright.

These results show that the solvent action of the drying oils is very small even after the lapse of several months. If there is anything to choose between them, tung oil would appear to have the advantage.

2. NON-DRYING FATTY OILS.

An important series of results with certain well-known non-drying fatty oils has been given by Marcy[1] who exposed nearly 3 grm. of iron to their action for a period of ten days. The numerical results obtained are given in the following table:—

ACTION OF NON-DRYING FATTY OILS UPON IRON.

Oil.	Initial Weight of Iron. Grm.	Loss in Weight. Grm.	Relative Solvent Action.
Olive	2·1830	0·0025	100
Sperm	2·2788	0·0012	48
Neatsfoot	2·2096	0·0011	44
Cotton-seed	2·7205	0·0009	36
Castor	2·7054	0·0007	28
Lard	2·2645	0·0005	20
Almond	2·2560	0·0004	16
Rape	2·5180	0·0000	0

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[1] Marcy, "Engineering News," 1893, **30**, 78.

These results exhibit only moderate agreement with those obtained by Tucker,[1] who exposed iron to the action of various oils for a period of twenty-six hours only. The relative positions of the oils with regard to solvent action are, according to this investigator:—

Sperm oil	which	dissolved	0·0740	grm.	of iron	per litre
Olive oil	,,	,,	0·0624	,,	,,	,,
Lard oil	,,	,,	0·0240	,,	,,	,,
Castor oil	,,	,,	0·0068	,,	,,	,,

It will be observed that the relative positions of sperm and olive oils, and of lard and castor oils, are reversed.

A series of tests extending over twelve months has been carried out in America at temperatures ranging from 50° to 80° F.[2] It was found that tallow attacked iron most vigorously, and seal oil least so.

3. HYDROCARBON OILS.

The action of the hydrocarbon lubricating oils is a study of great importance, but has been strangely neglected, until comparatively recently. Tucker[3] exposed iron for twenty-six hours to the action of valvoline, cylinder oil (specific gravity, 0·921) and lubricating oil (specific gravity, 0·915) and found that no appreciable solution had taken place.

D. Holde[4] has published the results of an extensive research into the action of various oils, used as lubricants, upon iron. He gives the palm to Scotch thin fluid mineral oil, and further illustrates the very variable nature of the solvent action of different samples of the same kind of oil upon iron. For further details the reader is referred to the original work.

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[1] Tucker, paper read before "South Staffs Inst. Iron and Steelworks' Managers," 30 January, 1897.

[2] See "Engineering and Mining Journal," 1891, **51**, 632.

[3] Tucker, paper read before South Staffs Inst. Iron and Steelworks' Managers, 30 January, 1897.

[4] Holde, "Mitteilungen aus dem königlichen technischen Versuchsanstalten," 1895, **13**, 174.

XII.

THE PASSIVE STATE OF IRON.

It is well known that, when a strip of iron or steel is immersed in aqueous solutions of some copper salt, a deposit of copper is immediately produced, which adheres to the metal with more or less persistence, according to the particular conditions under which the experiment is carried out. Simultaneously an equivalent amount of iron passes into solution, the reaction being one of simple exchange between the two metals. Thus, if copper sulphate was the salt originally employed, an amount of iron sulphate will be formed equivalent to that of the copper salt decomposed. We may represent the reaction by the following equation :—

$$CuSO_4 + Fe = FeSO_4 + Cu$$

Schoolboys make use of this property to etch their names upon the blades of their penknives. The latter are coated with a thin layer of paraffin wax, and the desired initials scratched through this, whereby the bare steel is exposed. On dipping the blade into copper sulphate solution, the name is registered as a thin layer of copper upon the exposed parts, that portion of the iron protected by the wax remaining unchanged. Metallic silver may likewise be precipitated from solutions of its nitrate, and lead from lead nitrate.

In 1790 James Keir[1] made the remarkable observation that, when iron is placed in contact with nitric acid of specific gravity 1·45, it is "ennobled" or rendered "passive,"[2] and is no longer capable of precipitating metals from solutions of their salts; and this, to quote Keir's own words "without the least diminution of metallic splendour or change of colour".

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[1] James Keir, "Phil. Trans." 1790, **80**, 359.

[2] We owe the term "passive" as used in this sense to Schönbein.

It can scarcely be claimed, perhaps, that Keir was absolutely the first to make this observation. As early as 1777 Wenzel began his researches on the neutralization of acids by metals, and it is more than possible that the reaction between iron and nitric acid did not escape him. Further, Torbern Bergmann[1] knew that silver was not as a rule precipitated from strong nitric acid solutions of its salts by metallic iron, although in some few cases it was. After Bergmann, Kirwan[2] seems to have been the next to mention the subject in connexion with the precipitation of metallic lead from its salts.

The work of Keir, however, appears to have been forgotten during the next few years, and the phenomenon was rediscovered by Wetzlar.[3] The time was now ripe for a further study of the subject, and a number of investigators at once entered the field. It was soon found that passivity might be induced by immersing the iron in numerous other acids, such as, for example, chloric acid,[4] arsenic acid,[5] chromic acid,[6] iodic acid,[7] and by the employment of mixtures of two or more acids, or of acids and certain salts, such as sulphuric and nitrous acids, or a combination of these with potassium iodate, etc.[8] Nor is it absolutely essential that acids should be present in the passivifying liquid, for neutral aqueous solutions of silver nitrate,[1] lead nitrate, potassium permanganate, soluble bichromates, etc., will produce the same effect when suitable concentrations are employed. Ramann[2] observed that iron is readily made to assume the passive condition by using it as a positive electrode in an electrolyte containing water.

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[1] Bergmann, "The Quantity of Phlogiston in Metals". "Opuscula Chimica et Physica," 1779-88, **3**, 140.

[2] Kirwan, "On Phlogiston," London, 1789. "The Precipitation of Metals," p. 244.

[3] Wetzlar, "Schweigger's Journ." 1827, **49**, 470.

[4] Boutmy and Chateau, "Cosmos," Revue des Sceances, 1861, **19**, 117; Phillips, "Phil. Mag." 1848 (3) **33**, 509.

[5] Boutmy and Chateau, op. cit.

[6] Beetz, "Pogg. Annalen," 1844, **62**, 234; 1844, **63**, 420; 1846, **67**, 186, 286, 365.

[7] Phillips, op. cit.

[8] Schönbein, "Pogg. Annalen," 1838, **41**, 42; J. F. Daniell, "Phil. Trans." 1836, **126**, 114.

Further, vapours and gases may passivify iron under certain conditions. According to Varenne[3] this is true of compressed nitric oxide, and Renard[4] points out a similar fact in connexion with the vapours of concentrated nitric acid. This latter investigator also showed that the momentary heating of iron in air is often quite sufficient to render the metal passive.

Although the majority of the experiments which have been made in this connexion refer to iron containing carbon as an impurity, there can be no doubt that passivification is a property of the pure metal itself, since Lenz[5] showed that pure iron, prepared by electrolytic processes, is readily converted into the passive state under the same conditions.

TESTING FOR PASSIVITY.

Schönbein[6] used nitric acid of specific gravity 1·35 as a test for passivity. If, upon immersion in this acid, the iron was not visibly attacked, it was assumed to be passive. On the other hand, if bubbles of gas escaped, the metal was regarded as active. This was rather an illogical method of working, for Faraday and Schönbein[7] showed that nitric acid of specific gravity 1·35 could itself passivify iron. Further, Noad[8] drew attention to the fact that iron, rendered passive by immersion in concentrated nitric acid, is not attacked by nitric acid of specific gravity 1·204, although this latter vigorously attacks a piece of ordinary or "active" iron. Nevertheless, following the lead of Schönbein, the 1·35 acid test was persistently used by many investigators. Heathcote[1] employs nitric acid of specific gravity 1·2, and regards a rod as passive when, after immersing and shaking in the acid and then holding motionless, no chemical action can be detected at the surface by the unaided eye, the temperature of the acid being about 15°-17° C. The advantage of this method is that the 1·2 acid shows no tendency to passivify active iron, and only very slowly activifies passive iron, requiring from twelve to twenty-four hours for this, according to circumstances. The liability to obtain uncertain and contradictory results is thereby reduced to a minimum.

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[1] It is interesting to note that Bergmann distinctly states that iron does not precipitate silver from concentrated solutions of silver nitrate. See de Benneville, "J. Iron Steel Inst." 1897, II, 40; Senderens, "Bull. Soc. Chim." 1896, **15**, 691; 1897, **17**, 279; Keir, op. cit.

[2] Ramann, "Ber." 1881, **14**, 1430.

[3] Varenne, "Compt. rend." 1879, **89**, 783; 1880, **90**, 998.

[4] Renard, "Compt. rend." 1874, **79**, 159.

[5] Lenz, "J. Prakt. Chem." 1869 (1), **108**, 438.

[6] Schönbein, "Pogg. Annalen," 1836, **37**, 390, 590.

[7] Faraday and Schönbein, "Phil. Mag." 1836, **9**, 53, 122.

[8] Noad, "Phil. Mag." 1837 (3) **10**, 276; 1838 (3), **11**, 48.

PASSIVIFYING IN NITRIC ACID.

The process of rendering iron passive by immersion in nitric acid is very complex, and a study of the behaviour of this metal towards solutions of the acid of specific gravity ranging from 1·245 to 1·36 is exceedingly interesting.

When first immersed the metal is usually attacked with vigour; the action then begins to slacken, smaller gas bubbles being evolved, until what may be termed "the slowly dissolving condition" is reached. There is still no sign of passivity, however, so long as the iron is held motionless in the liquid.[2] Passivification may be readily effected, however, by shaking the rod, by lifting it in and out of the acid, by dropping it to the bottom of the containing vessel with a shock, or in some cases by removing the rod entirely from the acid. Beetz suggests that the motion of the acid serves to bring fresh acid into contact with the surface of the metal whereby passivification is accelerated. But this can only be a partial explanation at best, for, as Renard[1] has pointed out, the rod may become passive after removal from the liquid even after the film of acid has continued its action.

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[1] Heathcote, "J. Soc. Chem. Ind." 1907, **26**, 899.

[2] See St. Edmé, "Compt. rend." 1860, **51**, 507; Herschel, "Ann. Chim. Phys." 1833, **54**, 87; Schönbein, "Pogg. Annalen," 1836, **38**, 444, 492; "Phil. Mag." 1837, **10**, 267; Heathcote, "J. Soc. Chem. Ind." 1907, **26**, 899.

A rod in the slowly dissolving condition may be rendered passive also by contact with platinum or by making it the anode of an electric current in another way.

In 1823 Avogadro[2] drew attention to the fact that, when iron and bismuth are connected to a galvanometer and then plunged into concentrated nitric acid, there is a deflexion first in one direction and then in the other. In dilute nitric acid, on the other hand, this reversal does not take place, the initial direction in the latter case being the same as that observed in the concentrated acid, but persisting for an indefinite time. This would appear to imply that some chemical action has taken place before the metal has been rendered passive. The experience of Heathcote is that highly polished iron rods, which have been kept cool during the process of polishing, invariably exhibit a visible dulling of the surface upon immersion in even the strongest acid—a fact which may be regarded as additional support to the view that chemical action has taken place.

THE CAUSE OF PASSIVITY.

Now what interpretation are we to place upon these results? Remarkable though it may appear, a thoroughly satisfactory explanation of the phenomena connected with passivity has not as yet been forthcoming, although numerous and very varied theories have been advanced from time to time. This is no doubt largely attributable to the contradictory results obtained, not merely by different investigators, but by the same individuals, who have repeatedly found that two pieces of apparently similar iron under what are regarded as identical conditions do not always behave in the same manner. We shall now consider the more important theories of passivity, and endeavour to find out which is in most complete harmony with the main facts of the case, as we understand them at the present time.

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[1] Renard, "Compt. rend." 1874, **79**, 159.

[2] Avogadro, "Ann. Chim. Phys." 1823, **22**, 361.

1. *The Oxide Theory.*—Apparently the earliest explanation offered was that due to Schönbein, according to which a protective film of oxide covers the surface of the metal and thus renders it inert or passive, by preventing its coming into direct contact with reagents, much in the same way as a thin film of grease is known to prevent corrosion.[1] This view, since the year of its advancement, has gained an ever-increasing number of adherents. We do not at this stage need to commit ourselves as to the exact nature and composition of the oxide formed, nor even to assume that a weighable or visible quantity is produced. The simple assumption that the layer is sufficiently continuous and unbroken to protect the metal is all that is required. We shall have occasion to refer to this again later.

2. *The Gaseous-film Theory.*—Not a few are inclined to believe that passivity is due to an adhering surface film of gas, which protects the iron from acid attack. That gas may be oxygen,[2]

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[1] In 1836 Schönbein wrote to Faraday calling his attention to certain phenomena to be observed when iron is immersed in strong nitric acid or in a concentrated solution of silver nitrate, and suggesting oxidation as the cause, coupled with the existence of an electric state different from that of the normal metal. In handing this letter over to Mr. Phillips, at that time editor of the "Philosophical Magazine," Faraday added a number of observations of his own. See Schönbein and Faraday, "Phil. Mag." 1836 (3), **9**, 53 and 122; 1837, (3) **10**, 175; "Pogg. Annalen," 1836, **39**, 342. Schönbein, "Pogg. Annalen," 1836, **37**, 393; 1836, **38**, 444; 1838, **41**, 42; 1838, **43**, 1; 1843, **59**, 149 and 421. Beetz, see references, p. 182. A. von Martens, "Pogg. Annalen," 1844, **61**, 121. G. Wetzlar, "Schweigger's Journal," 1827, **49**, 470; 1827, **50**, 88 and 129. Noad, "Phil. Mag." 1838 (3), **11**, 305. Faraday, "Experimental Researches," Vol. II, p. 231. Schönbein, "Das Verhalten des Eisens zum Sauerstoff," Basel, 1837.

[2] Osann, "Pogg. Annalen," 1855, **96**, 498. De Regnon, "Compt. rend." 1874, **79**, 299. Muthmann and Frauenberger, "Zeit. Elektrochem." 1904, **10**, 929; "Sitzungsberichte der Kgl. Bayerischen Akademie," 1904, **34**, 201.

nitric oxide,[1] or nitrogen,[2] according to circumstances. Thus Fredenhagen points out that iron, which has been rendered passive by anodic polarization in sulphuric acid, behaves differently from that which has been immersed in concentrated nitric acid, and suggests that in the former case the metal is covered with a layer of gaseous oxygen, but in the latter with an oxide of nitrogen.

3. *The Physical Theory.*—Passivity is attributed by many to a physical alteration in the surface of the iron, although the precise nature of the change is a disputed point. According to Keir[3] and Senderens,[4] passivity is due to the formation of a layer of allotropic iron, and De Benneville[5] and Hittorf[6] apparently share the same view, although the latter is particularly guarded in the manner in which he expresses himself. This, of course, is reasonable enough as far as it goes, for we know that allotropic modifications of certain elements exhibit a greater divergence from one another in their physical properties, than do many pairs of entirely distinct and separate elements. Thus, for example, red phosphorus and the diamond appear to be much farther removed from yellow phosphorus and amorphous carbon, respectively, than do the metals sodium and potassium from one another. And it is easy to understand how an allotropic modification of iron might exhibit inertness or passivity towards those reagents which readily attack the ordinary variety.

On the other hand, such an explanation can scarcely be said to go to the root of the matter, for we may reasonably ask—

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[1] Mousson, "Pogg. Annalen," 1836, **39**, 330. Varenne, "Compt. rend." 1879, **89**, 783; 1880, **90**, 998; "Ann. Chim. Phys." 1880 (5), **19**, 251; **20**, 240. Fredenhagen, "Zeit. Physikal. Chem." 1903, **43**, 1; 1908, **63**, 1; "Zeit. Elektrochem." 1905, **11**, 857; 1906, **12**, 797.

[2] St. Edmé, "Compt. rend." 1861, **52**, 930; 1888, **106**, 1079.

[3] Keir, "Phil. Trans." 1790, **80**, 359.

[4] Senderens, "Bull. Soc. Chim." 1896 (3), **15**, 691; 1897 (3), **17**, 279.

[5] De Benneville, "J. Iron Steel Inst." 1897, II, 40.

[6] Hittorf, "Zeit. Physikal. Chem." 1898, **25**, 729; 1899, **30**, 481; 1900, **34**, 385; "Zeit. Elektrochem." 1898, **4**, 482; 1899, **6**, 6; 1900, **7**, 168.

what is allotropy? The answer usually given is that, in allotropic modifications of the elements, the individual atoms are either arranged differently in the molecules, or are present in varying numbers, or possibly both. Of course absolute proof for this supposition is not available at present, for we have no means of obtaining an insight into the inner structure of solid matter. Nevertheless, the probability of such an explanation being a close approximation to the truth is very strong, particularly when we remember that this has been definitely proved to be the case for the gaseous allotrope of oxygen, namely ozone, O_3.

It will be clear that a rearrangement of the atoms in a molecule may be either accompanied by, or entirely independent of, a change of valency. Consequently those elements which are known to exhibit a variable valency have increased facilities for atomic rearrangement, and may therefore be expected to exhibit allotropy to a more or less pronounced degree. This is indeed true of phosphorus and carbon, to which reference has already been made, the former of which is sometimes trivalent and at other times pentavalent, whilst carbon is usually either divalent or tetravalent. It is a matter of common knowledge that iron forms two classes of salts, known respectively as ferrous and ferric compounds. In the ferrous condition iron is evidently divalent, and in ferric salts the metal has a valency of three. In the case of iron, therefore, any allotropy might very well be due to a rearrangement of the atoms consequent upon a change of valency. This brings us at once to the views of Krüger and Finkelstein[1] who incline to the belief that passive iron is the trivalent metal, whereas ordinary active iron is the divalent form. But what is valency? It would seem almost certain, from the most recent researches into the constitution of matter and the nature of chemical affinity, that valency is to be regarded as an electrical phenomenon.[2] If this be granted, the Krüger-Finkelstein theory practically amounts to postulating an electrical difference in the metal. This is evidently realized by Müller,[1] who bases his theory of passivity on the electronic hypothesis of metallic conduction. It is argued that a metal exhibits different phases according to its valency at the time, consequently any medium or material which can effect an alteration in the equilibrium existing between the electrons and metallic ions will have a corresponding effect upon the activity or passivity of the metal, as the case may be. As Fredenhagen[2] points out, if it were but possible for Müller to give definite proof to this hypothesis, a most important stride would have been made towards the solution of the difficulties connected both with passivity and with metallic conduction.

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[1] Finkelstein, "Zeit. physikal. Chem." 1902, **39**, 104.

[2] See Friend, "The Theory of Valency". Longmans & Co., 1909.

It is worthy of note that the various modifications of the physical theory of passivity agree in attributing passivity to a change induced within the metallic zone by external circumstances. The oxide and gaseous theories, on the other hand, postulate a change in the medium surrounding the metal, which is brought about in the former case at the expense of the metal itself, whereas, in the latter, the metal remains entirely unaltered.

Various other theories and modifications of theories have been advanced from time to time by different investigators. As, however, they are of minor importance, many of them having been proved to be wrong, we need not consider them here. The student, wishing to pursue the subject further, is advised to consult the literature to which references will be found at the end of the succeeding section.[3]

THE CHARACTERISTIC PROPERTIES OF PASSIVIFIED IRON.

It behoves us now to try and determine which of the above-mentioned theories will explain in the most satisfactory manner the various phenomena connected with the passivity of iron, which have been definitely established and are practically beyond dispute. It is very necessary to confine ourselves exclusively to such as these, for so many contradictory statements have appeared in the leading scientific journals from time to time that, unless special care be taken, we may find ourselves rejecting this theory or that, merely because it fails to explain some curious reaction which has never taken place save, possibly, in the imagination of some inaccurate observer and recorder.

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[1] W. J. Müller, "Zeit. physikal. Chem." 1904, **48**, 577; "Zeit. Elektrochem." 1905, **11**, 755 and 823.

[2] Fredenhagen, "Zeit. physikal. Chem." 1908, **63**, 4.

[3] See p. 199.

(*a*) In those cases in which passivity is induced by simple immersion of the iron in a liquid, *the latter is always a more or less powerful oxidizer*, as is evident from a consideration of the various passivifying media mentioned on p. 182. This at once suggests the oxide theory as offering the best explanation, for it is unnecessary to make any definite statement as to the composition of the particular oxide believed to be formed, as this constitutes a separate study in itself. But the other two theories are not necessarily at variance with this fact. The free oxygen liberated on the surface of the iron by contact with the oxidizer need not necessarily combine with the metal to form an oxide, for iron, as we have seen in an earlier chapter, may remain in contact with oxygen at ordinary temperatures and under suitable conditions for an indefinite time without undergoing any visible change. The necessary conditions are that no liquid electrolyte shall lie in contact with the metal, and this is certainly the case here if the gaseous film is sufficiently impenetrable, as we assume it to be. Further, the adherents of the physical theory argue, and with every reason, that an oxidizing liquid is particularly favourable to the formation of allotropic iron or for the electrification of the metal, according to the particular phase of the theory to which they lend their support.

(*b*) *Passive Iron does not always lose its Passivity in Vacuo.*— This is a problem about which much might be written were it desirable. Several investigators have stated that passive iron becomes active in vacuo. Thus Varenne[1] found that a piece of passive iron became active under a pressure of 15 mm. of mercury, and Belck[2] asserts that passive iron in nitric acid of specific gravity 1·2 becomes active in vacuo. The matter has been elucidated, however, by the careful experiments of Heathcote.[3] This investigator points out that, on evacuating a vessel containing iron immersed in nitric acid, bubbles of gas form on the surface of the metal and rise to the top of the liquid; but, although the mechanical action of these bubbles sometimes renders the iron active, it is more usual for a cessation of the bubbles to occur at an early period, and for the iron to remain quite passive for hours at a pressure of 15 mm. of mercury. It was observed, however, that sudden admission of air would sometimes activify the iron. Further, some iron rods were passivified by immersion in nitric acid of specific gravity 1·4, shaken, and transferred to a small vessel, that could be evacuated rapidly to a pressure of from 1 to 5 mm. of mercury. The rods soon lost all the adhering traces of nitric acid, and a few became active, but the remainder did not. When once dry the rods continued passive as long as they remained in vacuo, namely for one, fourteen, and even ninety hours.

In order to determine what effect an extremely high vacuum might have upon the passivity of iron, Heathcote introduced a dried rod of passive mild steel into a tube, together with some phosphorus pentoxide, to remove every trace of moisture. The tube was connected on the one hand with an evacuated vessel full of cocoa-nut charcoal and surrounded on the outside with liquid air. The other end led to an exceedingly delicate manometer, which admitted of being accurately read to 0·02 mm. A Plücker tube was also attached to the apparatus, which enabled any evolved gases to be examined spectroscopically.

On opening the tap connecting the tube containing the passive steel with the evacuated charcoal vessel, the pressure was almost instantaneously reduced to 0·026 mm. of mercury. The tap was then closed and the manometer slowly rose, indicating an increase of pressure due to the escape of gas from the metal. The actual figures obtained were :—

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[1] Varenne, "Compt. rend." 1879, **89**, 783.

[2] Belck, "Dissertation," Halle, a/S., 1888.

[3] H. L. Heathcote, "J. Soc. Chem. Ind." 1907, **26**, 899.

Time After Closing Tap. Mins.	Pressure. Mm.
0	0·026
2	0·082
5	0·132
11	0·180
16	0·208
73	0·268

The Plücker tube indicated the presence of air as the pressure of the gas increased. On removal, at the conclusion of the experiment, the steel was found to be still passive, and the same result was obtained on repeating the experiment.

It is obvious, therefore, that it is not the dissolved or occluded gases which are essential to passivity, and it is scarcely probable that any film of gas could remain unbroken on the surface of the iron after exposure to such a high vacuum for so long a time under the conditions of the experiment.

That some gas should have been evolved from the metal, when the containing tube was evacuated, is only what we might expect. Müller[1] observed that, on boring iron and steel, gases consisting chiefly of hydrogen were evolved. On heating the borings to redness in vacuo, only a little more gas was liberated, showing that it was chiefly mechanically enclosed or occluded within the pores of the metal. More recently Boudouard[2] has demonstrated the extreme tenacity with which these occluded gases cling to the metal, a third heating in vacuo to 1100° C. still yielding some gas. It is almost a pity that the steel used by Heathcote was not subjected to similar drastic treatment before passivification. Nevertheless his results serve their purpose, in that they prove conclusively that a passive metal does not of necessity become active in vacuo. Further, they throw considerable doubt upon the tenability of the gaseous film theory of passivity.

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[1] Müller, "Ber." 1879, **12**, 83; 1881, **14**, 6.

[2] Boudouard, "Compt. rend." 1907, **145**, 1283.

(*c*) *Iron may be Passivified without Suffering any Visible Change in Reflective Power.*—Reference has already been made to Heathcote's observation[1] that highly polished iron rods, which had been kept cool during the process of polishing, invariably exhibited a visible dulling of the surface upon immersion in even the strongest nitric acid. This is precisely what we might expect if we adhere to the oxide or gaseous film theory, and there is no reason why a physical change induced in the metal should not likewise produce an alteration in its external appearance. On the other hand, Müller and Königsberger[2] have measured the reflecting powers of iron mirrors immersed in alkaline solutions both in their normal condition, and also when polarized anodically and cathodically. Although the metal was sometimes active and sometimes passive, as was evident from E.M.F. measurements, the reflecting power always remained the same. The authors, therefore, conclude that passivity cannot be due to the formation of a layer of oxide. Such an argument is not conclusive, however. We do not need to suppose that a *thick* layer of oxide is formed around the metal. If it be of about molecular dimensions it will still serve to protect the metal and render it to a certain extent passive. But in order to affect the reflecting power, the film would require to have a thickness comparable with the length of a light wave, as Findlay[3] has pointed out. Krassa[4] assumes a similar attitude in criticizing the work of Müller and Königsberger, and concludes that a layer of oxide of sufficient thickness to cause passivity might not change the reflecting power of the metal by more than 2 per cent—an amount that could easily escape detection. The experiments of Müller and Königsberger therefore prove that, if an oxide layer is indeed the cause of passivity, then the film is exceedingly thin in the particular cases examined by themselves. Further than this we have no right to go. That this line of argument is perfectly reasonable is evident from the recent researches of Manchot.[1] This investigator draws attention to the fact first observed by himself and Kampschulte[2] that silver only reacts in ozone, in the cold, when a small quantity of oxide, either chemically deposited or mechanically attached, is present upon its surface. The behaviour towards 3 per cent ozonized air in the cold is therefore a sensitive means of detecting a film of oxide on silver and indeed on other metals, for a rapid darkening or discoloration is produced, even though the initial oxide film is so attenuated as to be indiscernible either by its appearance or weight. Manchot finds that iron, rendered passive by immersion in nitric acid and afterwards thoroughly washed, reacts almost instantaneously with ozone in the cold, as does iron rendered passive anodically in dilute sulphuric acid. On the other hand, active iron exhibits no such sensitiveness towards ozone. This appears to be as definite and decided an argument in favour of the truth of the oxide theory of passivity as we could desire.

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[1] See p. 185.

[2] W. J. Müller and J. G. Königsberger, "Zeit. Elektrochem." 1907, **13**, 659; 1909, **15**, 742; "Physik. Zeitsch." 1904, **5**, 415, 797; 1905, **6**, 847, 849; 1906, **7**, 796. Müller, "Zeit. Elektrochem." 1905, **11**, 823. Compare also F. Haber and F. Goldschmidt, "Zeit. Elektrochem." 1906, **12**, 49.

[3] A. Findlay, "Annual Reports of the Chemical Society," 1907, IV, 28.

[4] Krassa, "Zeit. Elektrochem." 1909, **15**, 490 and 981.

(*d*) *The Passivity of Iron is readily Removed by Heating in a Reducing Atmosphere.*—This fact is in thorough agreement with all three theories. If hydrogen is the reducing agent employed, water will obviously be formed whether we attribute passivity to a layer of oxide, or to a gaseous film of oxygen, or some gas containing oxygen. If nitrogen be the cause of the passivity as St. Edme[3] believes, ammonia gas will probably result, and the iron be thus rendered active again.

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[1] Manchot, "Ber." 1909, **42**, 3942.

[2] Manchot and Kampschulte, "Ber." 1907, **40**, 2891.

[3] St. Edme, "Compt. rend." 1861, **52**, 930.

Similar arguments apply to the activification induced by making passive iron the cathode in an electrolyte, and an explanation is thus forthcoming for the fact that when passive iron is immersed in nitric acid and touched with a strongly electropositive metal such as zinc, the iron acts as cathode and rapidly becomes active.

(*e*) *A Piece of Passive Iron is easily rendered Active by Simple Mechanical and Chemical Means.*—Thus, mere contact with water,[1] dilute nitric acid,[2] hydrochloric acid,[3] or sulphuric acid,[4] serves to activify the metal when in the passive condition. Schönbein [5] has also drawn attention to the fact that passive iron becomes active after a few seconds' exposure to potassium nitrate solution. In all of these cases the stirring of the liquid exerts a marked accelerating influence upon the rate at which activification takes place.[6] Further, the rate of action of a liquid upon the surface of passive iron may also be increased by heating, as perhaps we might expect if we are dealing with chemical reactions. That this is not due to the mechanical action of convection currents brushing past the passive surface has been demonstrated by Heathcote,[7] who sealed a piece of iron immersed in nitric acid of specific gravity 1·4, in a thick-walled glass tube. The last named was wrapped round and round with a cloth and very gradually warmed in water. Convection currents were thereby reduced to a minimum. After one and a half hours at 70° C. the iron became active, showing that the rate of activification is a temperature and not merely a mechanical effect.

It is interesting to note that merely touching a passive rod with active iron, zinc, or lead, when immersed in nitric acid, is sufficient to activify the first named. This, it may be remarked in passing, is due to electrolytic action. The passive iron is made the cathode on contact, and, if the oxide or gaseous film theory be regarded as true, the liberated hydrogen reduces the oxide or gas, exposing the under layer of active metal. Scratching with glass likewise removes passivity, and the activifying process is more rapid in proportion as the dilution of the acid adhering to the iron rod is increased. Finally, passivity disappears of itself in the process of time.

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[1] Keir, "Phil. Trans." 1790, **80**, 359; Buff, "Annalen," 1857, **102**, 265.

[2] Noad, "Phil. Mag." 1837 (2), **10**, 276.

[3] Schönbein, "Pogg. Annalen," 1836, **38**, 444, 492.

[4] *Ibid.* 1842, **57**, 63.

[5] "Phil. Mag." 1836, **9**, 53.

[6] See Renard, "Compt. rend." 1874, **79**, 159. Belck, "Dissertation, Halle a/S., 1888. Varenne, "Compt. rend." 1879, **89**, 783.

[7] Heathcote, "J. Soc. Chem. Ind." 1907, **26**, 899.

Curiously enough a magnetic field is also said to be an activifying agent.[1] Andrews draws attention to the fact that the passivity of iron increases with the concentration of the nitric acid. That induced by a solution of nitric acid of specific gravity 1·42 is regularly diminished as the temperature rises, until at 90° C. the "transition point" is reached, at which the metal becomes active. With very powerful magnetism the point of transition may be brought as low as 51° C.[2]

For several years the fact that a piece of iron gradually loses its passivity on standing was regarded as almost fatal to the oxide theory. Thus rods passivified in nitric acid of specific gravity 1·4 and exposed to the air were found by Heathcote to become active after a very varying number of minutes—sometimes six, at others twenty-five, and so on. This only refers to the moist metal, however. The recent researches of Manchot,[3] to which reference has already been made, throw an interesting side-light upon the question. Manchot finds that silver is readily covered with a remarkably attenuated film of oxide when exposed to the action of ozone at about 200° C. It would appear that this layer can be rubbed off, for it gradually disappears; and Manchot gives good reasons for believing that the adhesion of the oxide to the metal is gradually weakened, with the result that the former begins to flake off in minute layers, much in the same way as mill scale is known to separate from iron. It is not difficult to see how a similar action may take place with passive iron, and this at once overcomes the difficulty, particularly when we remember that it is only the *moist* passive metal which exhibits such a ready tendency to activification. Heathcote[1] has succeeded in preparing dry passive iron by rapidly spraying from a washbottle the following liquids in succession upon a rod of the recently passivified metal:—

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[1] Nichols and W. S. Franklin, "Amer. J. Science," 1889 (3), **34**, 419. T. Andrews, "Proc. Roy. Soc." 1890, **48**, 116. Nichols, "Amer. J. Science," 1886 (3), **31**, 272.

[2] Andrews, "Proc. Roy. Soc." 1890, **48**, 116; 1890, **49**, 120, 481; 1892, **52**, 114.

[3] Manchot, "Ber." 1909, **42**, 3942.

1. A saturated aqueous solution of potassium bichromate containing 2·8 grm. of potassium hydroxide per 100 c.c.

2. A mixture containing 100 c.c. of water, 10 c.c. of pure, methylated spirit, and 2·5 grm. of pure potassium hydroxide (by alcohol).

3. Absolute alcohol.

Dry passive iron was found to behave exactly as we might expect a metal covered with an oxide film to do. The rods were not rendered active by remaining even for several days in the ordinary atmosphere of a laboratory. Rubbing well with dry cotton wool had no effect, and contact with zinc and scratching with glass failed to activify those portions of the rods which were not touched.

(*f*) *Passive Iron is Soluble in Nitric Acid.*—According to many of the earlier investigators, iron when in the passive condition is insoluble in nitric acid. It has since been shown, however, that the contrary is true. Faraday[2] showed that a passive iron anode dissolves appreciably when an electric current is passed, and Belck[3] not only confirms this, but shows that the rate of solution depends upon the concentration of the acid, being less in more dilute acid.

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[1] Heathcote, "J. Soc. Chem. Ind." 1907, **26**, 899.

[2] Faraday, "Experimental Researches," 8th series, §§ 947, 996.

[3] Belck, "Dissertation," Halle a/S., 1888.

But not only during the passage of an external electric current does passive iron dissolve. After standing for a considerable time in fuming nitric acid green crystals of an iron nitrate are formed, showing that some of the metal has dissolved. It would appear from the researches of Gautier and Charpy,[1] that traces of ammonia and nitrogen peroxide are simultaneously liberated when the passive metal dissolves in nitric acid.

SUMMARY.

Numerous other phenomena, chiefly of an electrical nature, connected with passivity have engaged the attention of chemists and physicists during the past few years, but it is beyond the scope of this work to deal with them in further detail here. Sufficient has been said, however, to indicate the chief characteristics of passive iron, reference to the numerous doubtful and contradictory statements having been avoided for the reason given at the beginning of the chapter.

The reader will have observed that none of the theories advanced to account for passivity can as yet be definitely proved or disproved. We have, therefore, to rely, to a very large extent, upon what may be termed "cumulative evidence," a procedure which is not altogether satisfactory. However, for the present at any rate, we must content ourselves by selecting that theory which offers the most satisfactory explanation for the bulk of the phenomena, and accept it as a working hypothesis, until more facts have been brought to light, necessitating an alteration in our views.

At present the balance of evidence lies in favour of the oxide theory, which is now generally accepted in this country. It is, of course, possible that the passivities induced by different reagents are not always identical, but this is a point upon which no final decision can at present be made. If such is ever definitely proved to be the case, there is no reason why each and all of the theories discussed in this chapter should not be true for certain kinds of passivity. We have already mentioned that Fredenhagen[1] observes that iron which has been rendered passive by anodic polarization in sulphuric behaves differently from that which has been immersed in concentrated nitric. A difference in the kind of passivity is therefore assumed. On the other hand, a difference in the *degree* or *intensity* of passivification of the same kind might cause very marked differences in the behaviour of the metal. If the oxide theory is assumed to be correct, it is easy to see how variations in the thickness of the oxide layers would be very likely to influence the properties of the passive metal to a considerable extent.

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[1] Gautier and Charpy, "Compt. rend." 1891, **112**, 1451.

De Benneville[2] has brought forward a considerable body of evidence to show that the passivity induced by concentrated solutions of silver nitrate is identical in kind with that induced by strong nitric acid, the two differing from one another in degree or amount, only; and apparently Senderens[3] is of the same opinion. The latter investigator, however, draws attention to the fact that unannealed iron is more active than annealed iron, when both are immersed in nitric acid, as shown by electric measurements, but vice versa in silver nitrate—a fact for which a satisfactory explanation has yet to be found.

But we must leave this interesting branch of our subject[4] and pass on to a consideration of the possible composition of the oxide layer formed during passivification, assuming that the oxide theory is correct.

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[1] Fredenhagen, "Zeit. physikal. Chem." 1908, **63**, 1.

[2] De Benneville, "J. Iron Steel Inst." 1897, II, 40.

[3] Senderens, *ibid.* p. 78, in a letter commenting on De Benneville's paper.

[4] The reader, wishing to pursue his studies further in this direction, is recommended to consult the following literature, in addition to that already quoted in the preceding pages :—

Braconnot, "Ann. Chim. Phys." 1833 (2), **52**, 286; "Pogg. Annalen," 1833, **29**, 174.

G. T. Fechner, "Schweigger's Journal," 1828, **53**, 129; 1830, **59**, 113; "Pogg. Annalen," 1839, **47**, 1.

G. Wetzlar, "Schweigger's Journal," 1827, **49**, 470; **50**, 88, 129; 1828, **54**, 324; 1829, **56**, 207; 1830, **58**, 302.

Herschel, "Ann. Chim. Phys." 1833, **54**, 87; "Pogg. Annalen," 1834, **32**, 211.

Andrews, "Phil. Mag." 1838, **11**, 305.

Nature of the Oxide Formed.

Assuming, then, that the passivity of iron is caused by the formation of an attenuated film of oxide, the question naturally arises—What will its chemical composition be? Ramann[1] was of the opinion that the formula Fe_3O_4 might be attributed to it, in other words that it is the ordinary ferroso ferric oxide, hammer scale, or magnetic oxide. This opinion was based upon the belief that the oxide was soluble in dilute nitric oxide, but

A. von Martens, "Pogg. Annalen," 1842, **55**, 437, 612; 1844, **61**, 127.

Scheurer Kestner, "Ann. Chim. Phys." 1859 (3), **55**, 330; "Bull. Soc. Chim. Phys." 1862.

John Ordway, "Amer. J. Science," 1865 (2), **40**, 316.

Heldt, "J. prakt. Chem." 1863, **90**, 167, 257.

C. Thomlinson, "Trans. Chem. Soc." 1869, **22**, 125.

L. Schönn, "Pogg. Annalen," 1870. Supplement V.

Ramann, "Ber." 1881, **14**, 1430.

Wiedemann, "Lehrbuch Electr." 1894, II, 820.

Le Blanc, "Zeit. Elektrochem." 1900, **6**, 472; 1905, 11, 705.

Ostwald, "Zeit. Physikal. Chem." 1900, **35**, 33, 211. "Zeit. Elektrochem." 1901, **7**, 635.

Heathcote, "Zeit. Physikal. Chem." 1901, **37**, 368.

Mugdan, "Zeit. Elektrochem." 1903, **9**, 442.

Reuer, "Zeit. Physikal. Chem." 1903, **44**, 81. "Zeit. Elektrochem." 1905, **11**, 661.

Sackur, "Chem. Zeitung," 1904, **28**, 954; "Zeit. Elektrochem." 1904, **10**, 841; 1906, **12**, 637.

Boltzmann, "Zeit. Elektrochem." 1905, **11**, 9.

Gordon and F. E. Clarke, "Zeit. Elektrochem." 1906, **12**, 768; "J. Amer. Chem. Soc." 1906, **28**, 1534.

E. Müller and Spitzer, "Zeit. Anorgan. Chem." 1906, **50**, 321.

F. Haber and F. Goldschmidt, "Zeit. Elektrochem." 1906, **12**, 49.

Haber and Maitland, "Zeit. Elektrochem." 1907, **13**, 309.

Byers, "J. Amer. Chem. Soc." 1908, **30**, 1718.

J. Alvares, "Zeit. Elektrochem." 1909, **15**, 142.

Byers and Darrin, "J. Amer. Chem. Soc." 1910, **32**, 750.

[1] Ramann, "Ber." 1881, **14**, 1430.

not in strong, an assumption which would account for the activifying action of the former liquid, and for the passivity induced by the latter. Heathcote, however, finds that at ordinary temperatures the reverse is true, namely that the magnetic oxide is more soluble in concentrated acid than in dilute, and gives the following data:—

Specific Gravity of the Nitric Acid.	Weight of F_3O_4 Dissolved in 10 c.c.
1·4	0·02332 grm.
1·3	0·01752 ,,
1·15	0·01124 ,,

This observation, however, does not necessarily imply that the oxide layer causing passivity cannot consist of ferroso ferric oxide, as the following considerations will show.

It is generally assumed that the blue film which forms on the surface of iron heated in air to a temperature of approximately 290° C. is due to a layer of magnetic oxide. This may perhaps be true for the extreme outside portions, but for those nearer the metal Mosander[1] gives the formula $6FeO . Fe_2O_3$, that is, $5FeO . Fe_3O_4$. Mosander has shown, however, that the outer layers of thick oxide films, formed at higher temperatures, are nearly pure Fe_3O_4. Now whilst ordinary blued iron is not of itself passive, yet the darker the blue, the more rapidly can the metal be passivified; and rods, covered with a fairly thick layer of oxide by heating for fifteen minutes in the blowpipe, are quite passive to nitric acid of specific gravity 1·2 and to copper sulphate solution.[2]

These facts speak strongly in favour of the assumption that the oxide film causing passivity has the composition represented by the formula Fe_3O_4. No definite proof, however, is forthcoming.

Haber and Goldschmidt[3] incline to the belief that the film may be represented by the formula Fe_8O_{11}, that is $Fe_2O_3 . 2Fe_3O_4$, which oxide is shown to possess metallic conductivity.

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[1] Mosander, "Pogg. Annalen," 1826, **6**, 35.

[2] See Belck, "Dissertation," Halle a/S., 1888.

[3] F. Haber and F. Goldschmidt, "Zeit. Elektrochem." 1906, **12**, 49.

For all practical purposes, however, it is quite sufficient to assume that the relatively simple magnetic oxide, Fe_3O_4, is the one formed; and here we may conveniently let the matter rest, until we possess considerably more knowledge of the whole subject—a position which can only be attained by the vigorous prosecution of still further research upon this baffling, and therefore fascinating, subject.

THE ACTION OF CHROMIC ACID UPON IRON.

Allusion has already been made to the fact that aqueous solutions of chromic acid render iron and steel passive, and thereby inhibit the formation of rust. The author has kept pieces of pure iron foil, steel, and cast iron in contact with dilute solutions of chromic acid of varying concentrations for three or four years in sealed glass tubes, without the slightest change in external appearance being evident, save that in one or two cases, a slight local darkening occurred, which intensified with age.

That iron, which has been passivified in this way, is somewhat more resistant to corrosive agencies than the ordinary active metal is evident from the researches of Moody, Tilden, and W. H. Walker, to which reference has been made in an earlier chapter.[1] As we shall presently see, various suggestions have been offered for the protection of iron in commercial life by exposure to the action of aqueous solutions of soluble salts of chromic acid, or by coating the metal with paints and enamels containing insoluble chromates as pigments, whereby a precisely similar passive condition is engendered.

At first sight it seems a little strange that iron should be made more resistant to corrosion by the presence of chromic acid, when, as we have already seen, rusting is primarily the result of acid attack. But the difficulty at once disappears if we accept the oxide theory of passivity, and assume that the oxide formed is practically insoluble in the dilute chromic acid, and thereby protects the underlying metal from corrosion. Suppose, now, that we add a trace of common salt or sodium chloride to a solution of chromic acid in which a strip of iron is immersed, what will happen? From our knowledge of the behaviour of such mixtures we should expect a certain amount of free hydrochloric acid to be generated according to the balanced reaction:—

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[1] See Chapter V.

$$2NaCl + H_2CrO_4 \rightleftharpoons Na_2CrO_4 + 2HCl$$

and this, by dissolving the layer of oxide with the production of ferrous chloride, would expose a fresh surface of iron to attack. The ferrous salt in solution would then be further oxidized to ferric chloride and ultimately to rust at the expense of some of the chromic acid. That such is actually the case has been shown by Friend[1] who found that the addition of small quantities of a soluble salt of any mineral acid caused the rapid corrosion of the iron, a considerable amount of hydrogen gas being simultaneously evolved.

Evidently, therefore, the protection afforded by chromic acid to metallic iron is very limited in extent, too much so, in fact, to be of any practical utility at present, although, as we have seen in Chapter X., certain salts are useful for the purpose.

Bearing these various points in mind, one is led to ask whether solutions of pure chromic acid of any and every concentration will inhibit the corrosion of iron exposed to their action, or if a certain limiting concentration is essential, below which rusting may be expected to take place.

In order to answer this question Friend[2] bubbled a stream of pure, CO_2 free oxygen gas through solutions of chromic acid of various strengths contained in a series of small flasks. Strips of pure iron foil were placed in these, of total superficial area 8 sq. cm., with their four corners in contact with the walls and bottom of the flasks, in such a way that, as each bubble of oxygen passed through the liquid, it brushed the surface of the iron. After the lapse of two or three weeks, during which time the temperature remained fairly constant at 16° C., the appearance of the metal was noted. The results obtained are given in the following table:—

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[1] Friend, "J. Iron Steel Inst." 1908, II, 9.

[2] Friend, Carnegie Scholarship Memoir, entitled, "The Corrosion and Preservation of Iron," "J. Iron Steel Inst." 1911.

ACTION OF AQUEOUS SOLUTIONS OF CHROMIC ACID UPON IRON.

No. of Experiment.	Conc. of CrO_3 Grm. per Litre.	Molecular Conc. of CrO_3.	Appearance of Iron.
1	0·000	m/∞ [1]	Surface rusted in a few hours. Thorough corrosion after a few days.
2	0·019	m/5400	
3	0·028	m/3600	
4	0·037	m/2700	
5	0·056	m/1800	Two minute specks of rust after two weeks.
6	0·111	m/900	Surface of metal remained perfectly bright for several weeks, after which the experiment was stopped.
7	0·222	m/450	
8	0·333	m/300	

It will be observed that when the concentration of the chromic acid is not less than 0·11 grm. per litre, no visible corrosion of the iron occurs. This, therefore, is the limiting concentration[2] under the particular conditions of the experiments. The actual value of the limiting concentration varies somewhat according to circumstances such as, for example, the purity of the iron, its superficial area, and the temperature at which the experiments are conducted. The duration of the test is likewise an important factor, as a moment's consideration will show; for, during the course of a few weeks any corrosive action might be so slight as to escape detection, but after the lapse of as many years the corrosion might easily have proceeded to such an extent as to render itself not merely visible but readily measurable with the balance. No doubt, too, the ease with which oxygen can gain access to the solutions has also a bearing upon the value of the limiting concentration, and since mechanical agitation has been found to accelerate the activification of passive iron, it may also tend to assist its corrosion for that very reason. Friend found that when the flasks containing the iron and chromic acid were allowed to stand undisturbed and open to the air, instead of having oxygen bubbled through them, no rusting took place if the concentration of the chromic acid did not fall below 0·056 grm. per litre. That is to say the limiting concentration in these circumstances was only one half of that found in the previous experiments. This lower value is practically identical with that found by Heyn and Bauer,[1] namely 0·05 grm. per litre, who, however, used plates of iron measuring 3 × 4·5 cm. in area, but immersed them in a somewhat similar manner in solutions of chromic acid, allowing them to remain undisturbed for three weeks open to the atmosphere.

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[1] The symbol m signifies the molecular weight of the chromic acid expressed in grm. present in 1 litre of solution. The molecular weight of CrO_3 is taken as very approximately 100 grm.

[2] See p. 131.

The Solubility of Iron in Chromic Acid.—The question has often been raised as to whether or not iron is soluble in solutions of chromic acid. From the researches of Friend it would appear that the metal dissolves only excessively slowly in dilute solutions of the pure acid. After bubbling oxygen for several weeks through the small flasks containing iron foil and the various concentrations of chromic acid referred to above, not the merest trace of dissolved iron could be detected in any one of the liquids. In stronger solutions of chromic acid, however, iron dissolves with appreciable rapidity. Thus, the following results were obtained by immersion of two pieces of pure iron foil in saturated solutions of chromic acid exposed to the air at the temperature of the room :—

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitt. kgl. Material-prüfungsamt. Berlin, 1908, **26**, 73.

No. of Sample.	Duration of Experiment.	Area of Iron Foil. Sq. Cm.	Loss in Weight of Iron. Grm.	Remarks.
1	9 days	12·5	0·0022	Metal very dull. Rusted easily on immersion in water.
2	1 month	12·5	0·0080	

On adding ammonium hydroxide to the chromic acid solutions at the conclusion of the experiments, the characteristic reddish brown precipitate of ferric hydroxide was produced. This, on filtering off and dissolving in dilute hydrochloric acid, gave all the usual reactions of a ferric salt, thus clearly proving that the loss in weight sustained was indeed due to solution of the iron itself and not merely to that of any traces of manganese or other impurity which might have been present.[1]

THE ACTION OF CHROMATES AND OF BICHROMATES UPON IRON.

Solutions of soluble chromates and bichromates act upon iron surfaces in a precisely similar manner to those of free chromic acid itself. It is convenient, however, to consider these salts under a separate heading for reasons which will appear as we proceed.

Cushman[2] appears to have been the first to determine the limiting concentration of aqueous solutions of potassium bichromate, which protect iron against corrosion. Polished strips of steel were immersed in glass tubes open to the air and containing solutions of varying concentrations, ranging by regular dilutions from about 5 grm. down to 0·05 grm. per litre. At the end of two months it was observed that no rusting had occurred in any of the tubes containing 0·076 grm. of bichromate and more per litre, corresponding approximately to 2·5 lb.

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[1] See p. 137.

[2] A. S. Cushman, "The Corrosion of Iron," Bull. 30, U.S. Department of Agriculture, Washington, 1907.

in every 3000 gallons. Heyn and Bauer[1] and Friend[2] have independently confirmed this result. Cushman has further demonstrated the fact, since confirmed by Friend, that potassium bichromate solutions exert no appreciable solvent action upon pure iron, although manganese is readily dissolved by them. At the boiling temperature a higher concentration of bichromate was found to be necessary to cause complete protection of the metal, namely $\frac{1}{160}$ normal, that is, a solution containing 0·36 grm. per litre, equivalent to 10 lb. of bichromate in 3000 gallons. Cushman therefore suggests that the corrosion taking place in boilers might be greatly reduced by the employment of this limiting solution, namely by adding 10 lb. of bichromate to every 3000 gallons of water used.[3] It must be remembered, however, that just as is the case with the free chromic acid itself, bichromate solutions cannot protect iron against corrosion in the presence of free acids or of soluble salts. In the case of those boilers in which these latter are absent, however, Cushman's suggestion would appear to be very promising, and certainly merits a fair trial.

As we have already seen in an earlier chapter[4] Friend and Brown have studied the action of solutions of sodium chloride and potassium bichromate, both separately and when mixed in all proportions, upon plates of pure iron completely immersed in them. It was found that dilute solutions of bichromate, although unable to completely inhibit corrosion in the presence of sodium chloride, certainly protected the metal to a considerable extent, the best results being obtained when from 0·1 to 1·0 grm. of bichromate were present per litre of solution. With greater concentrations of bichromate, as for example 10 grm. of the salt per litre, a markedly greater corrosion was observed than with pure sodium chloride alone.

It is evident, therefore, that Cushman's proposed amelioration of boiler corrosion may prove of considerable value provided the concentration of the bichromate employed is not excessive, otherwise it may constitute an evil in itself, by aggravating the very offence it is intended to cure.

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[1] Heyn and Bauer, op. cit. 1908, **26**, 75.

[2] Friend, Carnegie Scholarship Memoir, "J. Iron Steel Inst." 1911.

[3] See note and correction, p. 161.

[4] See Chapter X.

On the other hand, the employment of the more insoluble chromates and basic chromates, such as those of lead (chrome yellow, orange chrome, etc.) and zinc (zinc chrome or citron yellow) as pigments in paints to be applied to the surface of iron as a protection against undue corrosion, is to be heartily recommended. The value of this procedure has long been recognized, although the scientific principles underlying the same were, until quite recently, by no means well understood.[1] It is, of course, essential that the pigment should be free from soluble impurities such as stimulate corrosion, otherwise the painting may do more harm than good.

It has also been suggested that by passivifying iron and steel, as, for example, by washing with bichromate solutions, before covering with a protective paint, a surer safeguard against corrosion would be obtained. But the experiments of M. Toch [2] indicate that this is no advantage, for after six months no difference could be detected in the extent of corrosion of steel coated with a good protective paint, and steel first rendered passive and then coated with the same kind of paint.

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[1] See Wood, "Trans. Amer. Soc. Mech. Engineers," 1895, **16**, 671; Cushman, "Proc. Amer. Soc. Testing Materials," 1908, **8**, 605; "J. Iron Steel Inst." 1909, I, 23.

[2] Toch, "Trans. Amer. Electrochem. Soc." 1909, **14**, 207.

XIII.

THE INFLUENCE OF CHEMICAL COMPOSITION UPON THE CORRODIBILITY OF IRON.

UNTIL quite recently this branch of our subject, although of paramount importance, had been singularly neglected. Scores of investigators have busied themselves with experiments devised to determine whether iron or steel is the more reliable metal, some few, only, having the good sense to give analyses of the metals used. The result is that scientists, manufacturers, and consumers, alike, have involved themselves in endless disputes, each bringing forward a mass of genuine data in support of his arguments. It is said that every religion under the sun could be proved to be the only true one by quoting suitable isolated and disconnected passages from Holy Writ; and it would seem that every variety and shade of opinion, relative to the superiority of iron or steel over the other, could be substantiated by experiments made upon pieces of metal chosen at random. Nor is the explanation far to seek. Steel is a very complex mixture, so that not only do two specimens made by different processes usually differ from one another in a marked degree, but even two different batches from the same plant exhibit variations. Now metallurgists know that the merest traces of impurity suffice to alter very materially certain of the physical properties of the iron, so much so that fractions of a per cent of sulphur, phosphorus, and the like, have to be carefully estimated. The same truth applies, although to a less rigorous extent, with regard to susceptibility to corrosion, and it is consequently of little use to draw rash conclusions from tests conducted with samples of iron and steel exhibiting of necessity differences in composition, until the actual effect of each of these variations has been separately determined. Now this latter can only be done by starting with a metal of high purity, and introducing one, and only one, new constituent in varying proportions at a time, and testing the products so obtained.

In the present chapter an attempt has been made to give an account of all the reliable work which has hitherto been done in this connexion[1] and the careful reader cannot fail to be struck with the incompleteness of our knowledge. Here is a wide field for research, with a certainty of securing useful results. Who will step into the breach?

The introduction of foreign elements into steel may alter the corrodibility of the same in a variety of ways:—

1. Some elements, such as, for example, sulphur, when present in steel exist in the form of relatively oxidizable compounds. Thus sulphur exists almost exclusively as manganese sulphide, and this readily undergoes oxidation whereby sulphureous acids are produced, which stimulate corrosion to an enormous extent.

2. Other elements combine directly with the iron forming alloys which are very stable and capable of resisting oxidation to a high degree. This would appear to be the case with nickel and silicon.

3. The presence of foreign elements along with iron when in the molten condition tends to produce segregation, or unequal distribution of the materials, during the process of solidification, whereby galvanic activity is stimulated, and the liability to corrode proportionately increased.

Here, then, we have an explanation for some of the conflicting results which have puzzled different investigators, and the reader, by bearing these points in mind, will readily understand the irregular and apparently anomalous behaviour of certain of the elements which we are now about to consider.

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[1] The literature upon the subject is, however, very scattered, being not infrequently indexed under other headings, and it is just possible that a few omissions may occur. The author believes, however, that any such will be of but minor importance, for every effort has been made to bring the chapter up to date.

ARSENIC.

The effect of alloying this element with iron has never been satisfactorily studied in so far as corrosion is concerned. According to Berthier [1] arsenical alloys of iron are more readily corrodible than the pure metal. Heyn and Bauer [2] have recently attacked the problem, but their results are not final, as they themselves admit, although they appear to support Berthier's statement.[3] Having no alloy of arsenic and iron available, Heyn and Bauer heated pieces of steel, measuring 2·3 × 1·8 cm. in area, and 0·6 cm. in thickness, in an atmosphere of arseniuretted hydrogen for one-and-a-half hours at a temperature of 900° C., a porcelain tube serving as the containing vessel. Similar pieces of steel were likewise heated in an identical manner, for purposes of comparison, but without the passage of arseniuretted hydrogen. The specimens were next polished and suspended by means of glass hooks in 1 per cent sulphuric acid solution, the loss in weight being determined in the usual manner. As a result it was found that the specimens which had been heated in arseniuretted hydrogen were much more vigorously attacked than those not so treated.

As the authors point out, however, the superficial impregnation with arsenic as obtained by the above process does not necessarily correspond in its resistivity to corrosion with homogeneous alloys of arsenic and iron. Further research upon this question therefore seems desirable.

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[1] Berthier, "British Association Reports," 1838, p. 265.

[2] Heyn and Bauer, "J. Iron Steel Inst." 1909, I, 109.

[3] I have not been able to find any other reference to Berthier's work than the one already quoted. Heyn and Bauer do not refer to Berthier and are evidently surprised at their own results, as they believed an alloy of arsenic and iron would be very resistant to corrosion. Why they should have expected such is not clear.

CARBON.

The influence of this element upon the rate of corrosion of iron is by no means as well understood as one could wish. The reason is not far to seek. Carbon can exist in iron in such a variety of forms, and alter its physical properties to such an extent that strictly comparable cases are not easy to arrange.

Take, for example, the number of forms in which carbon occurs in cast iron, constituting a continuous series ranging from martensite to kish. For the sake of convenience it is usual to recognize four distinct varieties, namely :—

1. *Primary Graphite*, which is produced at high temperatures and separates in flakes, more or less clearly defined.

2. *Secondary Graphite*, which differs from the former in that it exists in a very fine state of division,[1] and is sometimes known as "temper" carbon, owing to its having been first recognized by Ledebur in malleable cast iron.

3. *Combined Carbon* or *Carbide Carbon*, which occurs in a variety of forms, such as martensite, troostite, sorbite, and pearlite.

4. *Missing Carbon*, a special variety of combined carbon which is evolved as hydrocarbons on treatment of the metal with cold hydrochloric acid.[2]

Now in each of these forms the carbon exerts its individual influence upon the metal, and it does not follow that, because two samples of pig or cast iron contain the same percentages of total carbon, and of any other elements, therefore they will corrode at the same rate, for the relative amounts of the different forms of carbon may be so varied as to lead to uncertain results.

Similar remarks apply to steel, but in this case the problem is certainly simpler because this metal is far less composite in character than cast iron.

Heyn and Bauer[3] have recently thrown a flood of light upon this problem by a very thorough research, the results of which were brought before the Iron and Steel Institute of London about two years ago. We may therefore pass on at once to a consideration of the same.

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[1] Ledebur, "J. Iron Steel Inst." 1889, I, 386.

[2] See T. W. Hogg "J. Iron Steel Inst." 1896, II, 179.

[3] Heyn and Bauer, "J. Iron Steel Inst." 1909, I, 109.

The Influence of Quenching and Tempering of Hard Steel on its Solubility.

In carrying out these experiments a hard steel was employed having the following composition :—

Carbon	0·95	per cent
Silicon	0·35	,,
Manganese	0·17	,,
Phosphorus	0·012	,,
Sulphur	0·024	,,

It was in the form of a square forged bar, 2·5 × 2·5 cm. in cross section, from which slices were cut, 6 mm. in thickness, and subjected to the following treatments :—

1. Heated to 900° C. and quenched in water at 14° to 18° C., untreated.
2. Heated to 900° C. and quenched in water at 14° to 18° C., reheated at 100° C.
3. Heated to 900° C. and quenched in water at 14° to 18° C., reheated at 200° C.
4. Heated to 900° C. and quenched in water at 14° to 18° C., reheated at 275° to 305° C.
5. Heated to 900° C. and quenched in water at 14° to 18° C., reheated at 405° to 415° C.
6. Heated to 900° C. and quenched in water at 14° to 18° C., reheated at 500° C.
7. Heated to 900° C. and quenched in water at 14° to 18° C., reheated at 600° to 640° C.
8. In the original forged state.
9. Heated to 900° C. and allowed to cool slowly.

After the above treatment, the several samples were polished and immersed in a 1 per cent sulphuric acid solution and the loss in weight determined at the end of twenty-four, forty-eight, and seventy-two hours, respectively. The results obtained are given graphically in Fig. 53. In criticizing the same we cannot do better than quote the words of the authors:—

"The shape of the curve in Fig. 53 reveals some startling features. According to the opinions hitherto prevailing, and still held by some, the transition of the martensite of hardened steel into the pearlite of annealed steel is continuous throughout the intermediate stages of tempering. This would lead one to suppose that the curve of solubility in dilute sulphuric acid, instead of showing any sharply defined peaks, would form a line indicating the gradual transition from the solubility of martensite to that of pearlite. The curve, however, runs up to a sharply defined maximum at a temperature of 400° C. The

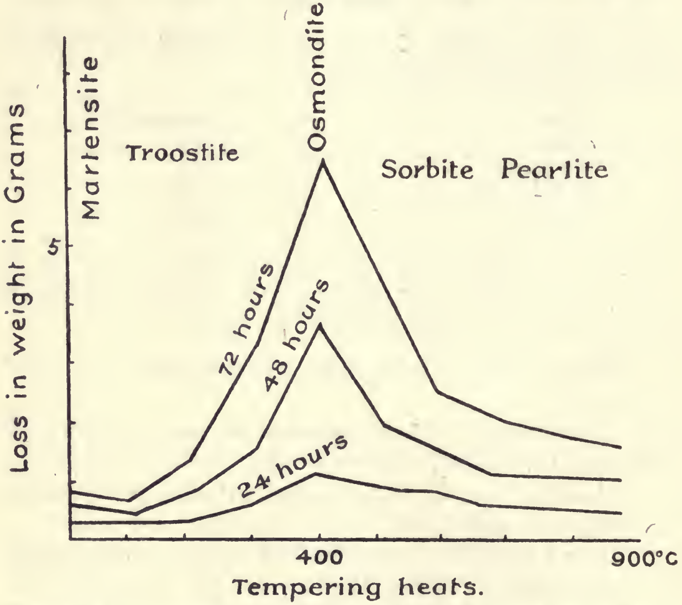

Figure 53.—Solubility of Tool Steel in Dilute Sulphuric Acid after being Tempered at Various Temperatures.

simplest and most obvious explanation of this phenomenon is as follows: The transition of the martensite from the unstable phase below 700° C. into the stable phase of pearlite, due to tempering, does not proceed directly, but indirectly through an intermediate metastable form, to which the name of osmondite has been given by the authors in honour of the celebrated investigator Osmond. Osmondite is the most soluble of all the forms intermediate between martensite and pearlite. As the tempering temperature gradually increases, the martensite first gradually changes into osmondite, until at 400° C. the whole mass consists of this alone. In order to prevent confusion in nomenclature, the term troostite has been hitherto retained by the authors for the designation of the intermediate states between martensite and osmondite, and for the stages intermediate between osmondite and pearlite they have continued to use the term sorbite. If the tempering temperature is raised above 400° C. there again occurs a gradual transition from the readily soluble osmondite to the less easily soluble pearlite. Such transitions from a preliminary condition to a stable final condition, through one or more less stable intermediate conditions, are of not infrequent occurrence in physical and chemical processes. As an instance may be mentioned the combustion of hydrogen, which, according to Nernst, is not burnt direct to water, but proceeds indirectly through the medium of the less stable peroxide.

"Another remarkable point in Fig. 53 is the lowest value for the solubility at a tempering temperature of 100° C., which differs little from that of untempered steel. The variation lies, however, within the margin of error for the process, so that whether still another metastable intermediate form occurs is not yet proved."

From the above it is clear that the particular condition in which the carbon occurs in the steel exerts an enormous influence upon the rate of solution of the metal in acid, and hence upon its general rate of corrosion.[1] A similar series of experiments was carried out with mild steel, analogous results being obtained. The percentage amount of carbon present was only 0·07, nevertheless the presence of the osmondite made itself evident by its increased solubility in acid. No very definite results were obtained from a study of the influence of the quenching temperature alone on mild steel, although it would appear that one minimum and two maximal solubility points exist, the two latter occurring at the quenching temperatures of 850°-950° C. and of 1100°-1250° C. respectively, and the minimum at 1000°-1050° C. Experiments with chromium-tungsten tool steel, containing 4·43 per cent of chromium, and 22·82 per cent of tungsten, exhibited a most pronounced maximum solubility at 1200° C. A close connexion between the hardness and the solubility was likewise noted, the hardness decreasing with the solubility.

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[1] See pp. 273-6 where the connexion between these two phenomena, namely resistance to acid attack and to corrosion is discussed in detail.

From the above it is clear that the mere determination of the amount of combined carbon in steel is not of itself sufficient to give any clue to the solubility of the metal, or its liability to corrode. It is essential that we also know the past history of the steel, so that an idea may be obtained as to the particular manner in which the carbon is combined. This is a new aspect of the question, and illustrates once more how complicated is the nature of the subject under discussion.[1]

CHROMIUM.

Seventy years ago Berthier[2] drew attention to the fact that alloys of chromium and iron are less corrodible than iron itself; and apparently modern experience bears this observation out.

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[1] Reference should here be made to the work of Howe, "Trans. Amer. Soc. Testing Materials," 1906, p. 158. Sang, "Proc. Eng. Soc. West Pa." **24**, p. 258. Ledebur, "J. Iron Steel Inst.," 1878, I, 15. Parker, "J. Iron Steel Inst.," 1881, I, 39; from which it is generally concluded that the resistance offered by steel to corrosion increases with the hardening carbon.

[2] Berthier, quoted by Mallet, "British Association Reports," 1838, p. 265.

R. A. Hadfield[1] has shown that the presence of small amounts of chromium increases the resistivity of the alloy towards acids to a remarkable extent. Samples of steel containing varying proportions of chromium, and measuring 2·5 × 0·5 inches in area, and 0·25 inch in thickness, were immersed in 50 per cent. sulphuric acid for a period of twenty-one days. The losses in weight sustained thereby are given in the following table:—

THE ACTION OF 50 PER CENT SULPHURIC ACID UPON CHROMIUM STEEL.

Metal.	Composition.		Loss in Weight. Per cent.	Colour after Treatment.
	Per cent C.	Per cent Cr.		
Chromium steel	0·27	1·18	3·32	Bright in some parts.
,, ,,	0·77	5·19	4·78	Tarnished.
,, ,,	0·71	9·18	5·64	Dull.
Ordinary mild steel	—	—	7·48	Bright.

The above results bring out the remarkable fact that, by increasing the percentage of chromium beyond a certain minimum amount, the resistivity of the steel towards acid attack decreases. It is highly desirable that the whole subject be investigated more thoroughly, and that experiments be performed, extending over longer periods of time, with the metal containing varying quantities of chromium exposed to general atmospheric and aqueous corrosion. The results obtained with sulphuric acid do not always coincide with those obtained by other methods, and this for reasons which will be explained in the next chapter.

It is quite possible that the resistance offered towards general corrosion by chromium steels is attributable to the formation of a thin protective skin of oxide in much the same way as is known to obtain with pig iron. This is rendered all the more probable by its remarkable freedom from scale on tempering in water, a feature to which Boussingault[1] drew attention a quarter of a century ago. The oxide formed during heating adheres to such an extent that, in order to anneal the steel, it must be cleaned with a file to allow of judging its colour.

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[1] Hadfield, " J. Iron Steel Inst." 1892, II, 92.

COPPER.

For many years it was believed that copper was a most undesirable element to be alloyed with iron, as cupriferous steels were observed to corrode considerably more rapidly than others.[2] Later researches, however, have shown that such is not of necessity the case, and that the corrosion of the earlier cupriferous steels was due, not to their copper content *per se*, but to the sulphur invariably associated with the copper.

F. H. Williams[3] appears to have been one of the first to show in a quantitative manner that a small percentage of copper increases the resistivity of iron to corrosion. Samples of Bessemer steel containing varying quantities of copper were exposed to the atmosphere for about a month, during which period they were soaked with water several times daily. The results obtained are condensed in the following table:—

	Loss per cent.
1. Soft Bessemer Steel	1·85
2. ,, with 0·078 per cent copper . . .	0·89
3. ,, with 0·145 ,, ,, . . .	0·75
4. ,, with 0·263 ,, ,, . . .	0·74

Stead and Wigham[4] have obtained similar results for iron wires containing copper. Weighed portions of the wires in fourteen gauge were placed in a wooden frame side by side, and immersed in a tank through which a constant stream of Middlesbrough town water circulated. After a period of nine weeks the wires were removed, cleaned, and weighed, with the following results :—

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[1] Boussingault, "J. Iron Steel Inst." 1886, II, 807.

[2] Karsten ("British Association Reports," 1838, p. 265), however, more than seventy years ago classed the copper alloys along with those less liable to corrode than ordinary iron.

[3] Williams, "Iron Age," 29 Nov. 1900, from "Proc. Eng. Soc. Western Pennsylvania," 1900, **16**, 231.

[4] Stead and Wigham, "J. Iron Steel Inst." 1901, II, 122.

CORROSION OF CUPRIFEROUS STEELS (STEAD AND WIGHAM).

	Composition of Metal. Per cent.						Corrosion. Per cent.
	Carbon.	Manganese.	Silicon.	Sulphur.	Phosphorus.	Copper.	
Series I.	0·990	0·463	0·168	0·034	0·021	0·010	12·7
	0·970	0·491	0·177	0·034	0·023	0·460	10·1
Series II.	0·430	0·940	0·065	0·030	0·063	0·025	10·6
	0·420	0·930	0·065	0·030	0·067	0·480	8·9
Series III.	0·480	0·933	0·070	0·047	0·084	0·033	12·0
	0·490	0·933	0·075	0·047	0·082	0·889	13·5
Series IV.	0·330	1·090	0·028	0·118	0·049	0·012	19·0
	0·320	0·640	0·028	0·055	0·048	1·286	11·5
Series V.	0·310	0·676	0·084	0·047	0·084	0·012	14·7
	0·290	0·676	0·084	0·044	0·082	2·000	4·7

It will be observed that, with the exception of the third series, the cupriferous steels were less corroded than the same steels without copper, the maximum resistance being obtained with 2 per cent of copper. Similar results were obtained on immersing the wires in the tidal river Tees at Middlesbrough, but the difference, although still in favour of the copper containing steels, was less marked than in the above cases. On treating the same wires in dilute acid, the copper-free samples invariably dissolved completely long before the others.

More recently a series of very interesting results has been published by Pierre Breuil,[1] a Carnegie Research Scholar during 1906-7. The tests were carried out on the cast metals in order to institute a comparison between those steels which could be rolled and those which could not. The experiments are not entirely complete, and no doubt the author will be publishing further results as time goes on. The apparatus employed is shown in Fig. 54. Each sample, in the form of a cube, rested in a glass funnel supported in a beaker, which was covered with a glass plate in order to avoid excessive evaporation. The corrosive liquid employed was dilute sulphuric acid in the proportion of approximately two parts of acid to one of water, by weight. Any salts formed collected at the bottom of the beaker and thus exerted no disturbing influences upon the corroding metal. The experiments lasted one month.

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[1] P. Breuil, " J. Iron Steel Inst." 1907, II, 1.

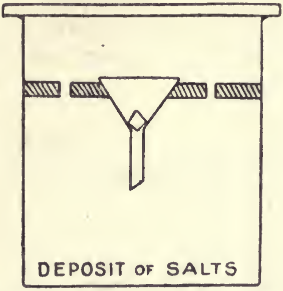

FIGURE 54.—BREUIL'S APPARATUS FOR DETERMINING THE RELATIVE CORRODIBILITY OF CUPRIFEROUS STEELS.

As a general rule it was found that the copper steels gave a white deposit of unknown composition which was more or less tinged with a reddish hue in proportion as the steels contained a greater or smaller amount of copper. The numerical results obtained are given in the following table, the loss in weight being taken as a measure of the corrosion :—

CORROSION OF CUPRIFEROUS STEELS (BREUIL).

		Percentage Composition of Metal.						Corrosion. Per cent.
		Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur.	Copper.	
Series I.	1	0·168	0·100	0·214	0·023	0·013	0·0	5·23
	2	0·158	0·092	0·223	0·016	0·017	0·490	4·40
	3	0·156	0·072	0·209	0·022	0·016	1·005	**2·80**
	4	0·165	0·108	0·214	0·023	0·017	2·015	3·01
	5	0·156	0·113	0·186	0·029	0·025	3·979[1]	3·34
Series II.	1	0·336	0·150	0·316	0·020	0·017	0·0	6·10
	2	0·390	0·139	0·323	0·020	0·018	0·505	3·54
	3	0·400	0·164	0·307	0·022	0·012	1·005	3·21
	4	0·389	0·175	0·242	0·023	0·010	2·025	**2·04**
	5	0·368	0·139	0·217	0·022	0·011	3·997[1]	2·50

[1] Average of two estimations given separately by Breuil.

As will be seen, the minimum loss occurs in the first series in the case of those steels containing 1 per cent of copper, and in Series II with 2 per cent of copper. The actual extent of corrosion in these cases is so slight as to make the steels rank in value with nickel steels in this respect. The results of experiments with steels containing still higher copper contents are to be awaited with interest. It would almost appear, however, from the results given above that such may prove less resistant to corrosion, just as was found to be the case with chromium steels, as we have already seen.

Müller and Wedding,[1] and Dillner[2] have likewise studied the cupriferous steels. The two former investigators conclude that the reduced tendency to corrode exhibited by these steels is due to the separation of copper sulphide and copper in the form of protective shells chiefly around the ferrite crystals. The reader desirous of pursuing the subject further is referred to the original memoirs.

MANGANESE.

The effect of manganese upon iron has been the subject of much controversy during the past few years, and the general opinion appears to be that a reduction in its amount is desirable in the case of such metals as are destined to face usual atmospheric or aqueous corrosive influences. As is well known, manganese finds its way into Bessemer and open hearth steels during addition of the recarburiser, and is to be regarded as a normal constituent of steel.[3] The main object of the addition of manganese is to remove the sulphur, which, as we shall see later, has a most injurious action upon the steel. Only a relatively small proportion of the manganese added actually remains in the steel, the bulk of it passing into the slag along with the sulphur, as manganese sulphide. That portion left behind in the steel and combined with the sulphur is readily recognized, if it occurs in patches large enough, by covering the metallic surface with gelatine, containing an acid solution of a cadmium salt. The acid liberates sulphuretted hydrogen, resulting in the immediate precipitation of insoluble yellow cadmium sulphide within the pores of the gelatine.[1]

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[1] W. Müller and Wedding, "Stahl und Eisen," 1906, **26**, 1444.

[2] Dillner, *ibid.* 1906, **26**, 1493.

[3] Baikoff, "J. Russ. Phys. Chem. Soc." 1907, **39**, 399.

According to Mallet,[2] Berthier was one of the first to call attention to the increased corrodibility of iron induced by the presence of manganese, and this is supported by the observations of Snelus,[3] Siemens,[4] Finkener,[5] and others. Turner[6] mentions that certain samples of steel containing manganese, amongst the specimens in the University of Birmingham, corrode far more readily than any others. Cushman[7] has devoted considerable time to an investigation as to the cause of wire-fence corrosion in America. Numerous samples of old wire were analysed, and it was soon observed that the majority of those which had withstood corrosion satisfactorily were either entirely free from manganese or contained less than 0·2 per cent of it. The most corroded specimens in the majority of cases contained manganese to the extent of 0·4 per cent. There were certain notable exceptions, however, a few good samples having as much as 0·4 per cent of manganese.

In Cushman's Bulletin, however, no reference is made to the sulphur content of the metal, and it may well be that the supposed harmful effect of the manganese was in reality due to the sulphur, the former element losing its reputation by means of its bad companionship, in exactly the same way as we have seen copper did.

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[1] See Law, "J. Iron Steel Inst." 1907, II, 94.

[2] Mallet, "British Association Reports," 1838, p. 265.

[3] Snelus, "J. Iron Steel Inst." 1881, I, 66.

[4] Siemens, *ibid.* 1878, II, 425.

[5] Finkener, "Mitteilungen aus dem königlichen technischen Versuchsanstalt," Berlin, 1897, **15**, 277.

[6] Turner, "Metallurgy of Iron," p. 421. Published by Chas. Griffin & Co., 1908.

[7] Cushman, "The Corrosion of Wire Fence". Farmer's Bull., 239. U.S. Department of Agriculture, 1905.

Heyn and Bauer[1] have recently published a few valuable quantitative data in this connexion. They secured a series of small iron plates, measuring 3·85 × 4·75 cm. in area, and 0·45 cm. in thickness, and immersed them in gas jars containing 200 c.c. of conductivity water. After twenty-two days the loss in weight was determined, the numerical results obtained, together with analyses of the metals used, being given in the following table:—

THE EFFECT OF MANGANESE UPON THE CORRODIBILITY OF IRON.

Percentage Composition of Metal.						Loss in Weight. Grm.	Relative Corrosion.
Total C.	Graphite.	Silicon.	Sulphur.	P.	Mn.		
3·45	2·97	3·06	0·059	0·072	**0·46**	0·0562	100
3·56	2·97	2·43	0·077	0·071	**0·70**	0·0515	92
3·66	3·17	2·56	0·076	0·072	**0·99**	0·0566	100
3·50	3·02	2·48	0·065	0·082	**1·90**	0·0525	94
3·70	3·10	2·61	0·052	0·082	**2·83**	0·0535	96
3·49	2·79	2·46	0·071	0·053	**3·08**	0·0500	89

As is evident from the above, the other elements present besides manganese are fairly constant in amount, so that any variation in corrodibility may reasonably be attributed to the action of the manganese. Unfortunately no parallel experiment was carried out with a metal entirely free from manganese, the lowest percentage of that metal being as high as 0·46. The results show considerable irregularity, and it would almost appear that variation of the manganese content between the above limits has but little effect upon the corrodibility of the metal, although the samples of highest manganese content show a slightly less corrosion than the others. The irregularities of the first four plates may be explained on the ground of irregular distribution of the manganese throughout the mass of the metal, which induces local galvanic action and consequent corrosion of varying intensity.

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[1] Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Materialprüfungsamt. Berlin, 1908, 26, 1.

Further research upon this interesting problem is highly desirable.

NICKEL.

The influence of nickel upon the corrodibility of iron has received a great deal of attention from chemists and metallurgists alike. Berzelius, the great Swedish chemist, was aware that nickel steels corrode less rapidly than most others. The fact that meteoric iron exhibits but little tendency to rust has been a matter of common knowledge for a long time, and analysis shows that such specimens invariably contain more or less nickel. In 1881, for example, a meteorite fell near Middlesbrough in Yorkshire, consisting of silicates interspersed with metallic particles, which latter contained :—[1]

Iron	76·99 per cent
Nickel	21·32 „ „
Cobalt	1·69 „ „
	100·00

Many other analyses might be given of meteorites found in different parts of the world bearing out the same fact, but the above is sufficient.

Now although the above data were undoubtedly convincing as far as they went, it was desirable to have quantitative data in addition, of a thoroughly reliable and systematic character.

In 1889 James Riley[2] read a paper before the Iron and Steel Institute, entitled, "Alloys of Nickel and Steel," during the course of which he pointed out that samples of steel, rich in nickel, had been lying exposed to the atmosphere and under his observation for several weeks, nevertheless they still exhibited an untarnished fracture. He further describes a series of experiments in which samples of nickel steel were immersed in

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[1] See "J. Iron Steel Inst." 1883, II, 716.

[2] Riley, "J. Iron Steel Inst." 1889, I, 45. The data given, however, are very sparse, which greatly reduces the value of the work.

Abel's corrosive liquid and in dilute hydrochloric acid. The two sets of results were thoroughly concordant, and the average is given in the following table:—

Metal.	Nickel per cent.	Relative Corrosion.
Mild steel	—	100
Nickel steel	5	83
,, ,,	25	1·15

The high percentage nickel steel is thus seen to be practically incorrodible.

Six years later, Wiggin[1] gave the results of a series of experiments in which the relative losses in weight of 3 per cent nickel steel and open hearth Bessemer steel were determined in two different ways:—

1. Polished specimens of the steel, measuring 1 square inch in area, and 0·25 inch in thickness, were immersed in 10 per cent salt solution in flasks, maintained for a period of three months at the boiling point, pure water being added at intervals to replace that lost by evaporation.

2. Similar pieces of steel were submitted to the action of steam at atmospheric pressure for two months.

At the conclusion of the experiments the metals were cleansed with a brush, washed with alcohol and ether, and finally weighed. The numerical results obtained are given in the following table:—

Metal.	Percentage Composition of Metal.						Relative Corrosion in:	
	C.	P.	Mn.	S.	Si.	Ni.	Salt Water.	Steam.
Nickel steel	0·27	0·006	0·77	0·10	0·014	3·03	**100**	**100**
Bessemer ,,	0·11	0·134	0·48	0·062	0·012	0	**181**	**215**
Open hearth ,,	0·15	0·01	0·60	0·009	0·007	0	**197**	**115**

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[1] Wiggin, "J. Iron Steel Inst." 1895, II, 164.

The greater resistance to acid corrosion offered by nickel steel in the above tests is patent. In discussing Wiggin's paper, Eaton, of the U.S. Navy, stated that the results of three independent sets of very complete American experiments showed that the relative corrosivities of nickel and carbon steel plates were as follows:—

Metal.	Nickel per cent.	Relative Corrosion.
Carbon steel	0·00	100
Nickel steel	0·0-2·0	100
,, ,,	3-4	95
,, ,,	10	Practically non-corrosive.

More recently Howe[1] has given the following data as representing the observed corrosion of nickel steel under different conditions:—

Metal.	Relative Corrosion in:		
	Sea Water.	Fresh Water.	Weather.
Wrought iron	100	100	100
3 per cent Nickel steel	83	80	67
26 per cent ,, ,,	32	32	30

Diegel[2] has determined the relative corrosion of plates of nickel steel half-immersed in sea water, contained in iron tanks. The plates measured 20 × 30 cm. in area and 0·6 cm. in thickness, and were exposed for a period of sixteen months, the water being renewed daily. The numerical results obtained are given in the following table; and are seen to be in good agreement with those of the previously mentioned investigators:—

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[1] Howe, "J. Iron Steel Inst." 1900, II, 567.

[2] Diegel, "Verhandlungen des Vereins zur Beförderung des Gewerbfleisses," 1903, **5**, 157.

Metal.	Nickel per cent.	Superficial Area of Metal. Sq. dcm.	Relative Corrosion.
Ordinary steel	0·02	12·45	**100**
Nickel steel	6·14	12·49	**65**
" "	29·68	12·48	**26**

From all these results it is clear that a nickel steel is particularly resistant to all classes of corrosive influences, its resistivity increasing with the percentage of nickel.

J. Divis[1] shows that the same is true in regard to nickel steel wires.

PHOSPHORUS.

The action of a phosphorus content on the resistance of iron to corrosion has not been made the subject of any very extensive experiments, although the general opinion appears to be that the presence of much phosphorus in steel is not desirable.[2] Whether this is due to the phosphorus *per se* or simply because it has not been evenly distributed throughout the mass of the metal, causing thereby galvanic action, is not clear.

Diegel[3] has experimented with plates of iron measuring 25 × 12 cm. in area and 0·7 cm. in thickness, containing varying proportions of phosphorus ranging from less than 0·01 to 0·85 per cent. The plates were suspended in large iron tanks and half-immersed in sea-water from Kiel harbour. The water was renewed daily by pouring over the upper half of the metal. After sixteen months the plates were cleaned and the loss in weight determined. The results obtained are given in the following table :—

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[1] Divis, "Oesterr. Zeit. Berg. und Hüttenwesen," **50**, 577, 594, 611, 626 and 636.

[2] Finkener, "Mitteilungen aus dem königlichen technischen Versuchsanstalt," Berlin, 1897, **15**, 277.

[3] Diegel, "Verhandlungen des Vereins zur Beförderung des Gewerbfleisses," 1903, **5**, 157.

THE INFLUENCE OF PHOSPHORUS UPON THE CORROSION OF IRON.

Percentage of Phosphorus.	Area Exposed. Sq. dcm.	Loss in Weight Sustained.
<0·01	6·35	44·40
0·09	6·36	38·83
0·23	6·36	36·37
0·45	6·36	34·87
0·84	6·35	32·77
0·85	6·35	31·35
0·062	12·45	74·47
1·08	12·53	60·66

Evidently, therefore, the addition of small amounts of phosphorus to iron retards the corrosion of the latter, when exposed to sea water, in a very marked degree, the resistivity increasing with the percentage of phosphorus. This is ascribed by Diegel to the formation of iron phosphide, which is capable of offering a fairly high resistance to the action of corrosive influences.

Heyn and Bauer have more recently carried out a few experiments with a view to determining the influence of somewhat larger quantities of phosphorus than those used by Diegel. Their results, however, show great irregularity, attributable no doubt to an unequal distribution of the phosphorus content.

SILICON.

For very many years chemists have been familiar with the fact that the presence of silicon tends to retard the corrosion of iron. Mallet[1] was aware more than seventy years ago that cast iron rich in silicon is not readily attacked by acids, Turner[2] draws attention to the fact that specimens of 18 per cent silicon pig have been exposed to the fumes of the laboratory at Birmingham University for many years without showing any appreciable quantity of rust. Jouve[3] shows that iron containing 20 per cent silicon is not attacked by acids, and should therefore exhibit but little tendency to corrode under ordinary atmospheric influences. Even when treated with nitric acid under the special conditions of high temperature and pressure of a Carius tube, the amount dissolved is exceedingly small. Hydrofluoric acid appears to be the only reagent which can be satisfactorily employed to effect its solution. When treated with hot sulphuric acid for two months, an alloy containing 20·6 per cent of silicon lost only 0·06 per cent in weight, but another sample containing 3 per cent of silicon lost 44·6 per cent, and some ordinary cast iron lost 46 per cent in weight in the course of two hours only. Other experiments quoted by Jouve are given in the following tables:—

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[1] Mallet, "British Association Reports," 1838, p. 277.

[2] Turner, "Metallurgy of Iron," p. 421. Pub. by Chas. Griffin & Co., 1908.

[3] Jouve, "J. Iron Steel Inst." 1908, III, 310.

ACTION OF 20 PER CENT NITRIC ACID UPON SILICON ALLOYS (APPROXIMATELY 20 PER CENT SI.).

Weight of Metal. Kilograms.	Loss or Gain in Weight after Twenty-Four Hours. Kilograms.	Loss or Gain in Weight after Forty-Eight Hours. Kilograms.
6·4410	−0·0392	−0·0599
5·1669	−0·0047	−0·0053
8·1524	−0·0037	−0·0069
14·5013	+0·0012	+0·0057
1·7060	−0·0716	−0·1039
1·4941	−0·0034	−0·0041

The weights of metal experimented upon will thus be seen to have a far greater mass than that usually handled by chemists, and the results are in consequence particularly valuable.

The slight increases in weight observed—and this is very noticeable when sulphuric acid was used, as the results given below will show—are attributable to the porosity of the metal and consequent saturation with acid or an acid product. It is impossible to expel this by heating owing to the crust of oxide which forms.

As still further illustrating the immunity towards corrosion by nitric acid, Jouve mentions that a pipe conveying 660 lb. of nitric acid vapour at 150°-200° C. for twenty-four hours had lasted from March, 1903 (presumably until the time of writing in 1908) and suffered a loss of weight amounting to only 3·5 oz. per 45 lb., or about 0·5 per cent.

ACTION OF VARIOUS ACIDS UPON SILICON ALLOY (APPROXIMATELY 20 PER CENT SILICON).

Acid used.	Twelve Hours' Exposure.		Twenty-Four Hours' Exposure.	
	Wt. of Metal. Kilograms.	Alteration in Wt. Kilograms.	Wt. of Metal. Kilograms.	Alteration in Wt. Kilograms.
Conc. HNO_3	13·9330	−0·0030	42·1690	−0·0060
HNO_3(1 : 1)	12·3262	−0·0030	38·6405	−0·0065
Conc. H_2SO_4	18·9060	+0·0222	32·6000	0·0000
H_2SO_4 (1 : 1)	14·3605	+0·0140	27·9800	0·0000
Tartaric	10·9270	0·0000	—	—
Acetic	6·2610	−0·0060	19·5632	−0·0090
Oxalic	10·6503	−0·0072	—	—

It would appear, therefore, that high silicon steels might be used with decided advantage in the construction of pumps, pipes, and other appliances with which acid, drainage, and other waters have to be handled, for ordinary cast iron is rapidly attacked by these.

Ferro-silicons containing from 40 to 90 per cent of silicon are attacked by moist air yielding poisonous gases as the civilized world has recently had occasion to learn; but the treatment of these does not fall within the scope of this work.

At this juncture attention should be called to a most interesting question raised by Carulla in connexion with the remarks of J. Wallace[1] of Bombay, who writes "I have seen native-made iron, forged on a stone anvil, and have observed that it does not rust like English iron when exposed to the weather. The iron work of the car on which the gods of the Kulu Valley take the air has a fine brown patina, and no rust flakes. It is all charcoal iron." Carulla[1] asks, "Can it be that the stone anvil mentioned by Mr. Wallace siliconides the skin of the Indian iron?"

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[1] Wallace, "J. Iron Steel Inst." 1908, I, 84.

Such an explanation sounds very plausible, and might also account for the remarkable freedom from corrosion exhibited by the ancient column at Delhi, to which reference was made in our opening chapter.

As regards corrosion, therefore, silicon alloys closely resemble those of nickel, for the greater the percentage of silicon the more resistant does the alloy become, until a practically incorrodible metal results containing 20 per cent of silicon.

Silicon, however, imparts to iron a number of peculiar properties and renders it difficult to work, so that unless its presence be confined to the surface of the metal by some method of after treatment, there seems little likelihood of a universal cure for corrosion arising from this source.

SULPHUR.

Sulphur is universally regarded as a stimulator of corrosion. Weinwurm[2] quotes the case of certain steel plates delivered to an Austrian Railway Company, which rusted with unusual rapidity. The cause was ultimately traced to the presence of no less than 1·08 per cent of sulphur, the manganese content being only 0·20 per cent. Now all sulphur is present in good steel as manganese sulphide, which latter substance is to be regarded as a normal constituent of steel.[3] In the case quoted by Weinwurm, however, there was only 0·20 per cent of manganese, whereas the total sulphur present could have combined with 1·86 per cent of that metal, showing that the steel was of an excessively poor quality.

The corrosive action of sulphur would appear to be twofold. By forming sulphides of relatively low melting-point, segregation is induced, and galvanic activity stimulated.[4] When once corrosion has set in, the sulphur oxidizes to sulphuric acid and further corrosion proceeds with increased velocity. An interesting example of this is given by Huntley.[1] It appears that corrosion had begun to manifest itself in a stand-by boiler at the generating station of the London Electric Supply Corporation. Attempts to check it by addition of caustic soda to the boiler water had proved unavailing. The interior of the boiler showed numerous blisters up to 30 mm. in diameter, most of them near the water level. Each blister contained a clear liquid with a black powder in suspension, and a pit was observed to be forming in the centre of each blister. Analysis showed that the liquid contained ferrous sulphate and free sulphuric acid, although the boiler water was alkaline and contained but little sulphur. The action was traced to the presence of manganese sulphide in the steel, which had become oxidized with formation of sulphuric acid. As the water in the boiler was quiet, the acid remained trapped behind a film of rust, and corrosion could thus rapidly take place, the oxygen required to convert the sulphur into acid penetrating the blister more readily than the alkali of the water. Addition of sodium arsenite to the boiler water in place of caustic soda completely stopped the trouble.[2]

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[1] Carulla, "J. Iron Steel Inst." 1908, I, p. 85.

[2] Weinwurm, "Chem. Zeitung," 1893, **17**, 101.

[3] Baikoff, "J. Russ. Phys. Chem. Soc." 1907, **39**, 399.

[4] See Chapter XIV.

OTHER ELEMENTS.

We have now considered the most important researches upon the subject under discussion in the present chapter. A few isolated facts, however, may be gleaned from the writings of different investigators as to the action exerted by a few other elements upon the corrodibility of iron, and these we may now pass on to consider.

Aluminium.—Calvert and Johnson[3] prepared an alloy of aluminium and iron by heating to whiteness a mixture of lime, aluminium chloride, and fine iron filings. The resulting product was very hard, and rusted on exposure to damp air. Analysis showed it to contain 12 per cent of aluminium.

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[1] Huntley, "J. Soc. Chem. Ind." 1909, **28**, 339.

[2] See p. 145.

[3] Calvert and Johnson, "Phil. Mag." 1855, **10**, 242.

Platinum.—Faraday and Stodart[1] found that alloys of iron and platinum containing 11 per cent of the latter metal are highly resistant to oxidation, exhibiting no corrosion after several months' exposure.

Rhodium.—Faraday and Stodart[2] found that an alloy containing 50 per cent of rhodium was capable of resisting corrosion for a long time.

Tin.—Percy[3] states that cast iron containing about 9 per cent of tin admits of a high polish, and is very rust resistant.

It is not without sincere regret that the author finds himself compelled to close this chapter in such an imperfect condition. But practically all has been said upon the subject that is at present known. Let us hope that the next few years will mark a rapid increase in our knowledge in this direction, for, until we understand the various influences exerted by the different elements, normally present in our commercial irons and steels, upon their rate of corrosion, we cannot hope to make much headway in the preparation of rust-resistant metals. When this has been thoroughly accomplished we shall be in a position to indicate what elements might be most advantageously introduced into steel and iron destined for certain particular purposes, and what elements should be avoided. Further, given a perfectly homogeneous sample, it should be possible, from a knowledge of its chemical composition, to assign a position to it on a standard corrosion scale.[4]

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[1] Faraday and Stodart, "Phil. Mag." 1822, p. 256. See Percy, "Iron and Steel," p. 177.

[2] Faraday and Stodart, loc. cit.

[3] Percy, "Iron and Steel," p. 160.

[4] See p. 276.

XIV.

ELECTRICAL AND GALVANIC ACTION.

Now although the terms Electricity and Galvanism are practically synonymous, it is advisable in this connexion to distinguish between the terms. To electrical activity we attribute the corrosion induced by currents of electricity arising from external sources, such as, for example, stray currents from the tramways, and so on, which are well known to be most destructive to iron work within their immediate neighbourhood. On the other hand, by galvanic action we mean the generation of local electrical activity by contact with the iron of a second substance in the presence of moisture. We shall now proceed to deal with each of the phenomena in detail.

Electrical Action.

As is well known, when an electric current passes through water, the latter is readily split up into its constituent elements, hydrogen and oxygen. Suppose, now, a bar of iron is embedded in the ground and surrounded by moist earth. The rate at which oxygen from the air can diffuse down to the metal will be excessively small, so that, unless the soil be unusually acid, the iron will remain uncorroded for an indefinite time. Wemlinger[1] mentions the case of a two-inch gas pipe which, although it had lain in the ground for twenty years, was in such an excellent condition of preservation that no sign of corrosion could be detected. No doubt the experience of many of my readers will substantiate this.

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[1] Wemlinger, "Engineering Contracting," 31, 20, 407.

The case is altered, however, if an electric current be passed through the system, for the iron and soil act as electrodes, decomposing the moisture into hydrogen and oxygen. The latter at once attacks the metal, forming rust, and corrosion proceeds apace. This is particularly true of wrought iron and steel, whereas, according to H. P. Brown,[1] cast iron is less affected in this way owing to the protective action of the adhering coating of moulding sand. He mentions, however, that in one case a cast-iron pipe was converted into a soft, black material, closely resembling graphite, and which could be easily cut with a knife.[2]

It is important to remember that, even when embedded in concrete, iron is not immune from the attacks of electricity. U. J. Nicholas[3] has made the subject a matter of careful investigation, and his results are of such far-reaching importance as to warrant their inclusion here :—[4]

1. Electrolytic corrosion of structural and reinforcing steel embedded in concrete takes place at the anode.
2. Even neat cement is no protection.
3. The cathode is not affected by oxidation.
4. Cement or concrete immersed in brine will crack when carrying an electric current to or from embedded steel.
5. Concrete conducts electricity electrolytically and not like a metal, its electric resistance being an inverse function of the percentage of sand.
6. It is found that even 0·1 ampere continuously flowing is sufficient to cause the destructive results indicated.

Bernauer[5] draws attention to the fact that the destructive action of stray currents may also be due to their heating power. This is mainly the case where short circuiting occurs, and is quite distinct from the effect of ordinary electrolysis.

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[1] Brown, "Electrical Engineer," New York, 1898, **26**, 441.

[2] See p. 169.

[3] Nicholas, "Engineering News," 1909, **60**, 710.

[4] For other references see pp. 236-8.

[5] Bernauer, "J. Iron Steel Inst." 1908, I, 389.

The cure for these evils is sufficiently obvious, for the presence of stray currents must be guarded against by keeping the return conductors in good condition. Tramways are the chief offenders and require particular attention. It will readily be admitted, however, that the practical solution of the problem may not always be easy—but that is the work of the electrical engineer, and does not concern us further. For other references to works and theses dealing with this subject the reader is referred to the subjoined list.[1]

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[1] Morse, "J. New England Water Works Association," 1893, **7**, 139.

Farnham, "Trans. Amer. Inst. Elec. Engineers," 1894, **11**, 191.

D. C. Jackson, "J. Assoc. Engineering Societies," 1894, **13**, 509; "Electrical World and Engineer," 1896, **28**, 684.

G. P. Low, "Trans. Amer. Inst. Elec. Engineers," 1894, **11**, 857.

C. A. Stone and H. C. Forbes, "J. New England Water Works Assoc." 1894, **9**, 25.

H. P. Brown, "Street Railway Review," 1895, **5**, 157; "Municipal Engineering," 1898, **16**, 84.

M. Hoopes, "Electrical World and Engineer," 1895, **25**, 603.

J. A. Fleming, "Zeitsch. Elektrochem." 1895, **5**, 241; "Electrician," 1898, **41**, 689.

Rowland, *ibid.* 1895, **25**, 127; "American Electrician," 1897, **9**, 156.

Brophy, "Electrical Review" (New York), 1896, **28**, 276.

J. Gray, "Electrical Review" (London), 1896, **38**, 3.

Haskell, "J. New England Water Works Assoc." 1896, **10**, 278.

C. Hewitt, "J. Franklin Inst." 1896, **142**, 51.

A. B. Herrick, "Engineering Magazine," 1898, **15**, 451; "Street Railway J." 1898, **14**, 186, 775; 1900, **16**, 472; 1901, **17**, 37; 1904, **23**, 516.

Abbott, "Cassier's Magazine," 1899, **16**, 371.

Barbillion, "L'Éclairage électrique," 1899, **21**, 94.

L. I. Blake, "Engineering Record," 1899, **40**, 239; "Electrical World and Engineer," 1899, **34**, 934.

F. A. W. Davis, "Municipal Engineering," 1899, **17**, 349; "J. New England Water Works Assoc." 1901, **15**, 225.

A. Knudson, "Engineering Record," 1899, **39**, 233; "American Electrician," 1900, **12**, 119; "J. New England Water Works Assoc." 1901, **15**, 244; "Trans. Amer. Electrochem. Soc." 1903, **3**, 195; "Engineering News," 1904, **52**, 437; "Cassier's Magazine," 1906, **30**, 337; "J. Franklin Inst." 1909, **168**, 132; "J. New England Water Works Assoc." 1909, **23**, 164.

GALVANIC ACTION.

This is a very large subject and one to which it is difficult to do full justice in the few pages at our disposal. It is hoped,

Adams, "Municipal Engineering," 1900, **18,** 1.
Brownell, "J. New England Water Works Assoc." 1900, **14,** 363.
J. Elder, "Elektrotechnische Zeitsch." 1900, **21,** 193.
Maury, "Engineering News," 1900, **44,** 38; 1903, **50,** 74.
Newbaker, "American Electrician," 1900, **12,** 72.
S. Sheldon, "Trans. Amer. Inst. Elec. Engineers," 1900, **17,** 335.
J. H. West, "Elektrotechnische Zeitsch." 1900, **21,** 706.
Wynkoop, "Popular Science Monthly," 1900, **56,** 357 (illustrated, showing the destructive action of stray currents).
Brigden, "Municipal Engineering," 1901, **20,** 287.
Ellicott, "J. Western Soc. Engineers," 1901, **6,** 526.
Leybold, "Electrical Engineer," London, 1901, **24,** 372.
McGowan, "Stevens' Institute Indicator," 1901, **18,** 163.
J. Swinburne, "Electrician," London, 1902, **49,** 642, 681.
Claude, "Elektrotechnische Zeitsch." 1902, **23,** 68.
Humphreys, "Electrical Engineer," London, 1902, **30,** 189; "J. Gas Lighting," 1902, **80,** 336.
Larsen, "Elektrotechnische Zeitsch." 1902, **23,** 841, 868.
Brophy and A. R. Gray, "Amer. Gas Light. J." 1904, **80,** 91.
Sever, "Trans. International Elec. Congress," St. Louis, 1904, **3,** 666.
Beadle, "Electrical Review," New York, 1905, **46,** 19.
Kinter, "Electric J." 1905, **2,** 668.
Stearns, "Engineering Record," 1905, **52,** 120.
P. A. Bates, "Engineering Record," 1906, **54,** 122.
F. Haber, "J. Gas Lighting," 1906, **95,** 578; "J. Gasbeleuchtung und Wasser Versorgung," 1906, **49,** 637.
F. Haber and Goldschmidt, "Zeitsch. Elektrochemie," 1906, **12,** 49; "Electrical Review," London, 1906, **59,** 446.
McLeary, "Electrical Age," 1906, **37,** 273.
Fernie, "Electrical Engineering," London, 1907, **1,** 1037.
Hayden, "Trans. Amer. Inst. Elec. Engineers," 1907, **26,** Part I, p. 231.
G. Rhodes, "Trans. Amer. Inst. Elec. Engineers," 1907, **26,** Part I, p. 231.
Ganz, "Trans. Amer. Electrochem. Soc." 1908, **14,** 151; "Proc. Amer. Gas Inst." 1907, **2,** 653.
Herdt, "Canadian Engineer," 1909, **18,** 197.
C. F. Burgess, "J. West. Soc. Engineers," 1909, **14,** 375.
Harper, "Ironmonger," 1909, **128,** 317.
Mott, "Amer. Electrochem. Soc." May, 1909.

however, that the following account will suffice to give the reader a grasp of the main points at issue, and that the subjoined references will enable him to obtain at first hand an acquaintance with the original memoirs from which much of the information contained in the present chapter has been gleaned.

The term galvanism has been loosely employed by numerous observers in order to explain all manner of curious cases of corrosion, oft-times as a shield to cover their ignorance of the whole question, with the result that much confusion has arisen. It may be well, therefore, at the outset to make perfectly clear what should be meant by the term galvanism, and then to try and determine in how far galvanic activity may be said to affect the rate of corrosion of metals. Suppose a plate of copper and one of iron are introduced separately into a vessel containing dilute sulphuric acid. At first very little occurs, a few bubbles of gas, only, escaping from the iron. These bubbles are hydrogen and are caused by the solution of the iron according to the general equation :—

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

If, now, we connect the two plates by means of a copper wire, and include a galvanometer within the circuit, as shown in Fig. 55, an electric current is seen to pass from the copper plate to the iron through the wire, as indicated by the arrow. Furthermore, the hydrogen bubbles cease to escape from the surface of the iron, and make their appearance upon the copper plate. The electric current is variously styled galvanic or voltaic, in honour of the two great investigators Galvagni and Volta, and is produced by the chemical energy set free by the solution of the iron. The copper plate, which may remain for an indefinite time unaltered within the cell, is known as the cathode, the iron being termed the anode. If, now, the copper

Siebel, "Ice and Refrigeration," 1909, **37**, 116.
Haber and Krassa, "Zeit. Elektrochem." 1909, **15**, 705.
Bergius and Krassa, *ibid.* 1909, **15**, 712.

be replaced by a plate of zinc, the galvanometer indicates that an electric current is flowing in the reverse direction, namely, from the iron to the zinc through the wire, and bubbles of hydrogen gas collect upon the surface of the iron, indicating that this metal now constitutes the cathode, and the zinc the anode, this latter metal dissolving, whereas the iron remains practically unaffected. The metals will obviously hold the same relationship to one another so long as they are in contact, irrespective of whether or not a galvanometer and copper wire are in circuit. It follows, therefore, that if two metals are brought into contact under conditions which might effect the solution of both of them separately, the probability is that only one of the metals will corrode, namely that which is at the higher potential and therefore constitutes the anode. If the initial difference in potential is but slight, reversals may easily take place, for reasons which will appear as we proceed, in which case both metals will corrode to an extent proportional to the time that each has served as anode. In either case the total corrosion is greater than that which would obtain if the plates were acted upon separately, not being in metallic connexion with each other. This is a point which has been frequently overlooked by investigators, and the explanation is, perhaps, not apparent at first. It is not difficult to understand, however, why such should be the case. Reverting to the simple cell composed of copper and iron plates immersed in dilute sulphuric acid, we see that, as the iron dissolves, chemical energy is set free; the equation :—

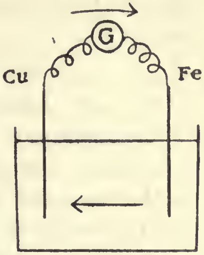

FIGURE 55.—A SIMPLE CELL.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

is therefore incomplete in so far that it takes no notice of this energy. When the iron is isolated, that is to say, when it is allowed to dissolve in the acid not being in contact with any other metal, this chemical energy is set free almost entirely as heat[1] so that the above equation might be more correctly expressed as :—

$$Fe + H_2SO_4 = FeSO_4 + H_2 + \text{Heat.}$$

The bulk of this heat is lost by radiation and in increasing the temperature of the sulphuric acid and the containing vessel. If we can so arrange matters that the loss by radiation is entirely avoided, and the amount of heat absorbed by the containing vessel and acid in raising the temperature through each degree is reduced to a minimum, the actual rise in temperature will become relatively great, with the result that the amount of iron dissolved in unit time will be proportionately increased. In practice, however, the loss by radiation is so great, and the heat capacity of the surrounding medium so large that in general no very great rise in temperature may be observed, and the iron dissolves at a relatively uniform rate. Almost the same result as is obtained by raising the temperature may be arrived at by connecting the iron with the copper by means of a wire. Part of the chemical energy liberated by the solution of the iron is now converted into electricity which is not lost by radiation as was the heat but stimulates the chemical action in a similar manner as an equivalent rise in temperature. Consequently, the iron passes more rapidly into solution even although the temperature remains substantially the same. It follows therefore that, whenever galvanic activity is induced, the total amount of corrosion is increased, although the actual extent of that increase must depend upon local circumstances. We shall have occasion to refer to this again several times in the sequel; meanwhile let us pass on to consider another point which, familiar though it may be to the electrician, has nevertheless been overlooked by students of corrosion.

It is incorrect to assume that, because a given metal is at a higher potential than a second metal when immersed in a certain liquid, therefore the same potential difference will be observed when any and every other liquid is employed; for such is not the case. The potential difference existing between a metal and an electrolytic solution depends not only upon the chemical nature of the electrolyte, but also upon its concentration, rate of motion[1] temperature, and the like. Now since this variation is not of necessity the same in either magnitude or direction for different metals, it follows that the differences of potential observed between two metals immersed in the same electrolyte under different conditions will not always remain constant. Furthermore, not only may this potential difference suffer change in degree, but even the polarity may, in extreme cases, undergo a reversal. For example, take the two metals copper and lead. When these are connected and immersed in dilute sulphuric acid a current of electricity is observed to pass from the copper to the lead through the wire, the copper serving as cathode and lead as anode. If now the acid be replaced by a solution of sodium sulphide, Na_2S, the direction of the current is reversed, the copper becoming the anode and the lead the cathode. In the former case, therefore, the lead would corrode and the copper remain intact, whereas in the latter case the lead would be preserved and the copper undergo corrosion. Herein is to be found an explanation for certain of the curious anomalies with which the literature of corrosion abounds, such as, for example, repeated reversals of polarity; and the careful reader cannot now fail to realize how essential it is that all the factors be thoroughly understood and detailed before conclusions are drawn as to the relative corrodibility and potential difference of any two samples of metal. We shall have several opportunities of discussing this important point in the sequel.

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[1] We are here assuming that the metal is perfectly homogeneous and pure, so that local galvanic activity is not induced at various points upon its surface—a condition of affairs which occurs largely with commercial irons.

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[1] These relationships have been carefully studied by Heyn and Bauer in their two classical memoirs: "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Material-prüfungsamt, Berlin, 1908, **26**, 2; 1910, **28**, 62. It is beyond the scope of this work to deal in detail with this aspect of their researches here, and the reader is referred to the original for the numerical data obtained.

For the sake of convenience we shall now pass on to consider the influence of galvanic activity in promoting and retarding the corrosion of iron under a variety of conditions.

A. GALVANIC ACTIVITY EXHIBITED BETWEEN STRAINED AND UNSTRAINED PORTIONS OF THE SAME PIECES OF IRON.

It has been found that galvanic activity may be induced by immersing two pieces of iron in an electrolytic solution, if one of the pieces of metal has been previously strained. We are indebted to T. Andrews[1] for a very thorough investigation of this branch of our subject, and we shall now proceed to consider his results.

1. *The Influence of Tensile Strain upon Corrosion.*—In order to determine this a bar of each metal to be tested was cut and turned to the dimensions shown in Fig. 56. It was then submitted to stress in a tensile apparatus, sufficient in most cases to induce an elongation of 20 per cent between the gauge points, situate some 3 inches apart. The piece was now cut in two at the centre and turned in a lathe until the unstrained ends marked A were of the same diameter as B. The two cylinders thus obtained were placed in a cell and covered to the depth of 0·75 inch with a saturated solution of common salt. They were held in position by insertion through two holes in a thick glass plate cover (Fig. 57), and were so arranged that the strained portion (B) of one bar and the un-

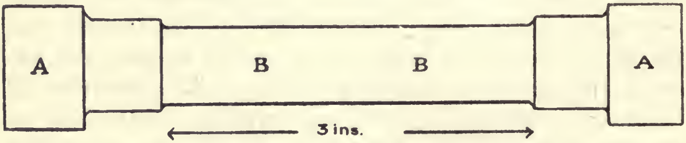

FIGURE 56.—BAR USED BY T. ANDREWS TO DETERMINE THE INFLUENCE OF TENSILE STRENGTH UPON CORROSION.

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[1] Andrews, "Min. Proc. Inst. Civil Engineers," 1894, **118**, 356.

strained portion (A) of the second bar dipped into the liquid. Metallic contact was made between the two cylinders only at the moment of reading the galvanometer. It was invariably found that a slight current flowed from B to A through the wire, that is to say, the strained portion was cathodic to the unstrained, the latter, therefore, being attacked the more vigorously. It can scarcely be urged that this is the result which we should have expected from *a priori* considerations. Hambuechen [1] has more or less closely repeated the work of Andrews, but concludes that the strained portions of the metal are anodic to the unstrained and are consequently more liable to corrode. This is exactly opposite to the conclusion arrived at by Andrews, and the question is: Who is right? The probability is that both are right, for Richards and Behr [2] have clearly shown that if a difference of potential does exist between the strained and unstrained portions, it must be extremely small, and largely governed by local circumstances.[3]

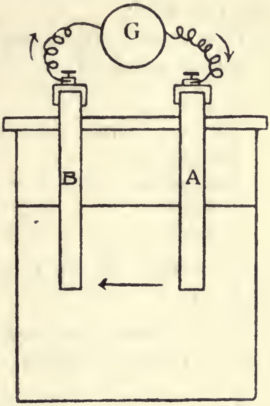

FIGURE 57.—CELL USED BY ANDREWS.

It is interesting in this connexion to call to mind the researches of Heyn and Bauer [4] upon the influence of stretching steel in the tensile testing machine on the solubility in dilute sulphuric acid.

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[1] Hambuechen, "Bull. Univ. Wisconsin," Engineering Series 8, 1900.

[2] Richards and Behr, "Publications Carnegie Inst." Washington, 1906.

[3] See also Walker and Dill, "Proc. Amer. Soc. Testing Materials," 1907, 7, 230. Burgess, "Trans. Amer. Electrochem. Soc." 1908, **13**, 17. The first-named authors support the results of Andrews. Burgess shows that test pieces which have been deformed by stretching beyond the elastic limit show a measurable difference of potential; his strained portions corroded more rapidly than the unstrained—a result which agrees with that obtained by Hambuechen.

[4] Heyn and Bauer, "J. Iron Steel Inst." 1909, I, 109.

To this end cylindrical bars of steel were taken, having the following composition :—

Carbon	0·07	per cent
Silicon	0·06	,,
Manganese	0·10	,,
Phosphorus	0·01	,,
Sulphur	0·019	,,
Copper	0·015	,,

and marked off into twenty equal parts, 1 cm. in length (Fig. 58).

The cylinder was now placed in the testing machine and stretched until it broke; the various divisions were now sawn through and the increase in length λ noted for each piece.

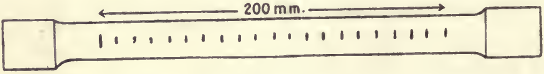

FIGURE 58.—MILD STEEL BAR USED BY HEYN AND BAUER TO DETERMINE THE INFLUENCE OF TENSILE STRESS UPON THE RATE OF SOLUTION IN DILUTE SULPHURIC ACID.

From these sections small test cylinders were turned, the axes of which coincided with the axis of the original bar, the diameters being 0·9 cm. and the lengths 1·0 cm. A similar cylinder was likewise turned to the same dimensions from the head of the bar which had not been stretched at all.

The cylinders were now subjected to the action of 1 per cent sulphuric acid, and the loss in weight determined after ninety-six hours. The losses in weight sustained are shown graphically in Fig. 59 by the continuous line, the broken line indicating the relative elongation. It will be seen that the greater the strain, the greater is the corrodibility. This result is therefore in accordance with the work of Hambuechen and of Burgess.

Numerous other experiments were carried out by Heyn and Bauer along similar lines, but for details of these the reader is referred to the original memoir.

2. *The Influence of Torsional Stress upon Corrosion.*—In order to determine this a bar of metal was turned by Andrews to the dimensions shown in Fig. 60. AB was submitted to torsional strain by turning B through an angle of 180°. The bar was

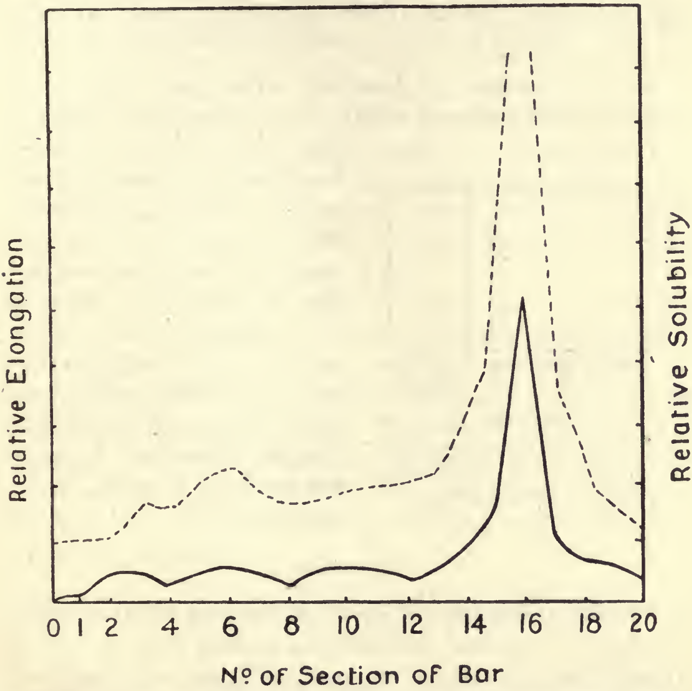

Figure 59.—Curve Showing the Influence of Stretching upon the Solubility of Mild Steel in Dilute Sulphuric Acid (Heyn and Bauer). (The Solubility of the Unstrained Steel is taken as 100.)

then cut in two at A, and both A (the unstrained portion) and B (the strained portion) were turned to the same dimensions, and finally immersed in sea water. As in his previous investigation Andrews found that the unstrained portion was anodic to the strained, and hence underwent more rapid corrosion.

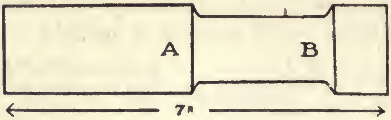

Figure 60.—Bar Used by T. Andrews in Determining the Influence of Torsional Stress upon Corrosion.

3. *The Influence of Flexional Stress upon Corrosion.*—Andrews used plates of metal of the dimensions shown in Fig. 61. All were polished bright and some bent (as shown on the right (Fig. 61) in the cold by strong pressure in a mould of wood, using soft padding to avoid surface abrasion. Upon immersion in saturated sodium chloride solution in a cell, the strained portion was again found to be less attacked than the unstrained, a current flowing from B to A through the wire.

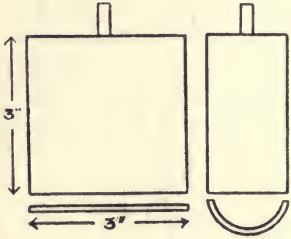

Figure 61.—Plates Used by Andrew to Determine the Influence of Flexional Stress upon Corrosion.

Summary.

From the foregoing it is clear that strain of any kind induces a change in potential, and that if a strained piece of iron be brought into contact with an unstrained piece, when immersed in an electrolytic solution, galvanic activity will be set up. The actual difference of potential is certainly very small and appears to be dependent upon local circumstances for its magnitude, so much so that it is difficult to say beforehand whether the strained or the unstrained portion will serve as cathode and thus be preserved at the expense of the other. The fact, however, that a difference of potential should exist at all should be made the subject of careful consideration not only by engineers in general, but also by manufacturers who, in their desire to increase the output of their steel, are apt to send that material into the market in a highly strained condition. Owing to the repeated rolling, etc., that wrought iron undergoes before it appears on the market, these remarks do not apply to it so much as to steel. We shall have occasion to refer to this again, however, in the next chapter. It will be obvious that all kinds of iron in service are liable to become strained, and an explanation is here to hand for the unusual tendency to corrode exhibited by indentations and abrasions on the surface of boilers. All the results dealt with in this section are consequently of no little practical importance. They are, moreover, exactly what we might expect, for strained iron differs from the unstrained metal in many other physical properties than those detailed above, as Andrews has clearly shown.[1]

It is well known that busy iron does not rust so readily as that which is allowed to lie idle. This is particularly true of railway lines.[2] Those which are being constantly passed over by trains are but slightly corroded, whereas the rails in disused sidings suffer enormous loss. Cushman's[3] explanation is ingenious, for it is based upon the assumption that the vibration and rushing of the trains over the metals breaks up any points of potential difference upon the surface, and thus reduces the tendency to corrode.

B. GALVANIC ACTIVITY EXHIBITED BETWEEN IRON AND ITS IMPURITIES.

If a piece of ordinary commercial iron or steel be allowed to corrode in water or in aqueous solutions of an electrolyte, it will be observed that the rusting takes place in patches, and not uniformly over the surface of the metal—and this in cases where differences of potential are little likely to have been set up by conditions of strain. This local action is greatly reduced by purifying the iron before exposure, and becomes negligibly small when plates of pure Kahlbaum's foil are employed, the coating of rust being remarkably uniform. Evidently, therefore, the presence of impurities on or near to the surface of the metal must be regarded as the initial cause of the local activity.

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[1] Andrews, "Min. Proc. Inst. Civil Engineers," 1886, **87**, 340; 1888, **94**, 180; 1891, **105**, 161.

[2] See p. 19 where other supplementary explanations are given for this phenomenon.

[3] Cushman and Gardner, "The Corrosion and Preservation of Iron and Steel," published by McGraw-Hill Book Co., New York, 1910, p. 108. See also W. Spring, "Bulletin Soc. Chim." 1903, **50**, 215.

The action which takes place, when impure iron is allowed to corrode, may be very beautifully shown by means of ferroxyl—a reagent devised by A. S. Cushman and W. H. Walker.[1] Cushman observed that whenever certain specimens of iron are immersed in water or in a dilute, neutral solution of an electrolyte, to which a sufficient quantity of phenol phthalein has been added, a pink colour is developed. If the solution is allowed to stand undisturbed for a time, it is observed that the pink colour is confined to certain spots or nodes upon the surface of the metal. Such spots are therefore cathodic, for here the iron does not pass into solution. Some specimens of steel exhibit this phenomenon more rapidly than others.

Since phenol phthalein shows only the cathodes, Walker[2] suggested the addition of a small quantity of potassium ferricyanide to the reacting solution, in order to furnish an indicator for the ferrous ions, whose appearance marks the positive poles, that is to say, the anodes. If iron passes into solution ferrous ions must appear, yielding with potassium ferricyanide the characteristic blue colour, known as Turnbull's blue. If the reagent is stiffened with gelatine diffusion is largely prevented, and the effects produced are rendered more permanent. Such a mixture is known as ferroxyl.

Cushman describes the preparation of ferroxyl as follows: "A 1·5 per cent solution of agar-agar is first made by dissolving a weighed quantity of powdered agar in the requisite amount of water. This solution is boiled for one hour, fresh water being added to replace that lost by evaporation. It is then filtered while hot, and 2 c.c. of standard phenol phthalein indicator added to every 100 c.c. of solution, after which it is brought to a perfectly neutral condition by titration with a $\frac{1}{10}$ normal solution of potassium hydroxide, or hydrochloric acid, as the case may be. The addition of 7 c.c. of a 1 per cent solution of potassium ferricyanide to every 100 c.c. of solution is then made, and the ferroxyl reagent while still hot is ready to use. Enough of the reagent should be poured into a Petrie dish just to cover the bottom and the dish floated in cold water until the agar has jellied. A clean sample of iron is then placed on this bed of jelly and covered with the hot solution. After the final addition of agar the dish should not be removed until thoroughly cooled. While the colours sometimes show up immediately, they usually require from twelve to twenty-four hours to attain their most perfect development. The mounts may be preserved for many months by keeping the surface of the agar covered with alcohol."

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[1] Cushman, "J. Iron Steel Inst." 1909, I, 33.

[2] Walker, "J. Amer. Chem. Soc." 1907, **29**, 1257.

Clearly, therefore, if we wish to retard the corrosion of iron we shall have to guard against irregularity of composition, and against the presence of traces of impurity upon the surface of the metal. Let us consider each of these points separately.

1. *Irregularity of Composition.*

It is well known that steels exhibited a decided tendency to segregate owing to the different temperatures of solidification of their constituents, and the lower the percentage of the iron, the greater is the tendency usually exhibited.[1] Now since the bulk of the impurities in the steel are electronegative to iron, it follows that differences of potential exist wherever segregation occurs, with the result that the metal exhibits an increased liability to corrode. Even soft Swedish steel bars show a marked irregularity in composition—more so, in fact, than is generally believed. W. Cobb[1] cites the case of one such bar which came under his own personal observation. The average carbon content as determined by analysis amounted to 0·04 per cent. When, however, microscopic examination was made of the cross section of the metal in various places, one portion of the bar was found to be practically carbonless, whereas another was almost saturated with carbon, containing presumably from 0·8 to 0·9 per cent of the element.

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[1] See Gaines, "Trans. Amer. Electrochem. Soc." 1908, **13**, 55. Marriott, "Min. Proc. Inst. Civil Engineers," **162**, 213.

No doubt those of my readers who have studied the microstructure of iron and steel can recall numerous instances of a similar nature which have come under their own personal notice.

Wrought iron has, of course, the advantage here, for it is piled, cross-piled, hammered, and rolled before being sent into the market, with the result that its composition is rendered much more uniform, and hence less liable to exhibit corrosion by galvanic activity.

If the iron is perfectly free from impurity, segregation cannot, of course, occur, and such metal should be particularly resistant to corrosion, unless it is placed in metallic contact with other metals, such as phosphorus and nickel steels, to which pure iron is electropositive and hence anodic. A striking example of this is afforded by the remarkably pure ingot iron which is now being placed on the market by the American Rolling Mill Co. of Middletown, Ohio, an analysis of which is given on p. 114. This metal contains 99·954 per cent of metallic iron, and when immersed in sulphuric acid undergoes solution with beautiful uniformity, the surface remaining practically smooth and free from the pittings which characterize even the best charcoal irons and usual grades of commercial steel when exposed to like conditions. The consequence is that, galvanic action being reduced to practically nil, the rate of solution of the iron in the acid is enormously retarded. Suppose, now, we could obtain absolutely pure iron; what then? Possibly it would be practically insoluble in acid. At any rate the recent researches of Lambert and Thomson[1] would seem to indicate that such a substance offers unusual resistance to corrosion.

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[1] Cobb, "J. Iron Steel Inst." 1909, I, 103.

2. *Surface Impurities.*

These may be divided into three classes :—

(*a*) Cinder, etc., present in the metal and disseminated as small particles throughout its mass, so that a certain amount will always manifest itself upon the surface of the metal. It would be difficult to remove this absolutely from commercial irons, but the American Ingot Iron Co., already referred to, has reduced its amount to an almost infinitesimal quantity, with the result that the metal shows none of the usual pitting when subjected to acid attack.[2] No doubt this metal will also prove highly resistant to corrosion in ordinary circumstances.

(*b*) Traces of oxide upon the surface of the metal are powerful stimulators of corrosion, and this is the more unfortunate since, during the manufacture of the metal, the iron is readily oxidized, yielding what is known as mill scale, which is very adherent and proportionately difficult to remove. As it is electronegative to iron, the free metal dissolves as the anode and corrosion proceeds apace.

The danger of leaving traces of hammer scale, or mill scale, as it is variously known, upon the surface of the metal about to be exposed to ordinary corrosive influences has been brought home to manufacturers in a variety of expensive ways. N. Barnaby[3] mentions that at Pembroke two ships were built and coated with anti-fouling composition before the mill scale had been completely removed. The amount of oxide left, however, was very small—negligibly so, as everybody believed. After the vessels had been at sea for some months, however, it was observed that rust had formed underneath the paint at the places where the oxide had not been completely removed, rendering it necessary to paint the ship afresh. At the present time the Admiralty removes every trace of oxide before painting its vessels, and the results fully justify this precaution. In this connexion White[1] mentions that the presence of black oxide left upon steel plates exposed to the action of sea water in Portsmouth harbour was found to cause serious pitting, and a pronounced difference of potential could be observed with a galvanometer. It is for this reason that many of the leading Bridge Companies abstain from painting their bridges upon erection, preferring to leave them to rust, whereby the adhering coat of mill scale is loosened. The metal is then scraped free from oxide more readily, and, when this has been carefully done, the bridge is painted thoroughly. In this way very satisfactory results may be arrived at.

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[1] Lambert and Thomson, "Trans. Chem. Soc." 1910, **97**, 2426.

[2] See p. 114.

[3] Barnaby, "Min. Proc. Inst. Civil Engineers," 1881, **65**, 104; "Trans. Inst. Naval Architects," 1879, **20**, 225.

The presence of rust itself is a powerful stimulant to corrosion,[2] but we are here concerned with it only in so far as it assists corrosion by its electronegative character. V. B. Lewes[3] has illustrated this in a striking manner. Some steel plates, measuring 4 × 1 inches in area, were cut from a sheet and polished on one side. On the polished surface of one plate a piece of thin blotting paper was laid so as not only to entirely cover it, but to project half an inch beyond its edges. It was then wetted with sea water and the polished surface of a second plate of steel placed upon it. The two plates were now connected by means of wires, a sensitive galvanometer being placed in circuit, and a deflexion of 20° on the scale was observed.

The upper plate was now smeared with a thin paste of magnetic oxide and sea water, and again connected. A deflexion of 112° was the result, showing an increased difference of potential.

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[1] White, "J. Iron Steel Inst." 1881, I, 68. See also Parker's Experiments, "J. Iron Steel Inst." 1881, I, 39, with discs of iron from which the hammer scale was not removed.

[2] See p. 96.

[3] Lewes, "Trans. Inst. Naval Architects," 1887, **28**, 247.

The magnetic oxide was now replaced by hydrated ferric oxide or rust, a deflexion of 65° being then observed, showing that rust is decidedly electronegative to steel, although not to such an extent as is hammer scale. Hydrated ferrous oxide gave a deflexion in a similar manner of only 25°, showing that its action is very little more than that of the two plates alone.

These experiments do not establish quantitatively the relative electrical relations existing between steel and its oxides, but they do show that rust is capable of setting up galvanic activity, although it is less intense in its action than is the magnetic oxide, and consequently slower in proportion. Schleicher and Schultz[1] have since studied the subject in greater detail, but the above suffices for our purpose. The Reader desirous of pursuing the study further is referred to the original memoir.

We are now in a position to understand the causes leading up to what is known as pitting, to which iron immersed in sea water is particularly liable. According to Lewes the action is started at some point by the presence of moist rust particles or other impurity, which is electronegative to iron. The hydrogen liberated by the galvanic current gently pushes up the protecting coats of paint, tar, etc., forming a small blister.[2] Sea water leaks in, an active electric current resulting, which leads to the production of more rust. In this way relatively large rust cones are formed. In many of these cones the structure is distinctly visible, showing them to be formed of successive layers, each layer pushing up the one above it.

(*c*) Artificial coatings applied to the surface of iron even when intended for purposes of protection are not infrequently sources of danger. This is particularly true in the case of paints, the pigmentary particles of which are coarse and unevenly distributed. The oil or binding material is never absolutely moisture proof, and the coarser particles of pigment are apt to induce galvanic activity underneath the paint, themselves constituting the cathode, the iron beneath oxidizing as the anode.

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[1] A. Schleicher and G. Schultz, "Stahl und Eisen," 1908, **28**, 50.

[2] A blister might also be caused by the expansion of the iron in oxidizing to form rust, quite apart from the liberation of hydrogen.

The obvious remedy is to employ a finely ground pigment thoroughly incorporated with the oil, and one which is not a good conductor of electricity. For this reason a mixture of rouge and lampblack, ground to an impalpable powder, and thoroughly mixed with pure boiled linseed oil with very little turpentine, may be recommended as a suitable paint, where protection of the underlying metal is the main object, and not its decoration. For obvious reasons such a paint should only be applied to the cleaned surface of the iron, and should be renewed whenever necessary, not being allowed to remain on the iron when its surface has broken and cracked.[1]

C. GALVANIC ACTIVITY EXHIBITED BETWEEN DIFFERENT KINDS OF IRON.

When plates of iron and steel are immersed in water, dilute acid, or aqueous solutions of metallic salts, and connected by means of a copper wire, a feeble current is found to pass from the one metal to the other. The actual direction of the current, however, varies according to circumstances. This phenomenon has been made the subject of careful investigation by several scientists. In 1882 J. Farquharson[2] published an account of a series of experiments carried out in Portsmouth harbour. Plates of iron and steel, having a total area of 48 sq. ft., were cleaned free from scale, and after being weighed were put into grooved wooden frames at a distance of 1 inch apart, the iron and steel alternating (Fig. 62). The first, third, and fifth pairs were electrically connected at the top by straps of iron, the others remaining free. After six months' exposure to the sea water the plates were removed, cleaned, and weighed, the results being given in the following table:—

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[1] The reader may be recommended to study in this connexion a contribution by W. H. Walker and Warren K. Lewis to the "J. Industrial and Engineering Chemistry," 1909, 1, No. 11, entitled "Paint and Varnish Coatings as Accelerators in the Corrosion of Metals".

[2] Farquharson, "Trans. Inst. Naval Architects," 1882, **23**, 143.

FARQUHARSON'S EXPERIMENTS.

No. of Pair.	Metal.	Loss in Weight. (Oz.)	Total Loss in Weight for the Pair. (Oz.)
1	Iron	7·869	8·759
	Steel	0·890	
2	Iron	3·681	7·389
	Steel	3·708	
3	Iron	7·160	7·779
	Steel	0·619	
4	Iron	3·396	7·396
	Steel	4·000	
5	Iron	6·000	8·702
	Steel	2·702	
6	Iron	4·123	8·450
	Steel	4·327	

A consideration of these data shows that:—

1. The isolated plates of iron and steel corroded at almost identical rates.

2. When the plates of iron and steel were in metallic contact, the former metal corroded far more rapidly than the latter.

3. The total corrosion exhibited by each pair of plates was slightly greater when they were in metallic contact than when isolated. The explanation for this has already been given.[1]

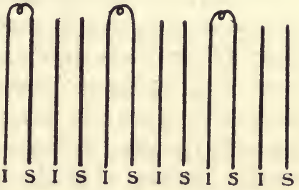

FIGURE 62.—ARRANGEMENT OF IRON AND STEEL PLATES IN FARQUHARSON'S EXPERIMENTS.

Other experimenters have found that in similar circumstances it is the steel which has become the anode and corroded the more rapidly. Assuming that the metals are fairly homogeneous in their composition this relative interchange of polarity may be accounted for in one or both of two ways, namely:—

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[1] See p. 240.

1. A difference in the liquid medium surrounding the metals. Attention has already been directed in an earlier section to the important part played by the liquid medium in determining the relative polarities of two metals. For example, copper is cathodic to lead in sulphuric acid, but anodic in solutions of sodium sulphide. Now in the case of iron and steel we are dealing with exceedingly slight differences in potential, so that proportionately small variations in the physical condition or chemical nature of the surrounding medium may be sufficient to induce a reversal of polarity.

2. A difference in the chemical compositions of the metals. We have already seen in an earlier chapter what an enormous influence upon the physical and chemical properties of iron and steel is exerted by the presence of even small amounts of foreign elements,[1] and that a corresponding change in potential should be induced is not to be wondered at. Now since a very slight alteration in the potential is sufficient to cause a reversal of polarity, it will be clear that, when we are dealing with such composite mixtures as modern steel and wrought iron, very slight differences in their composition will suffice to determine their relative polarity; and since two batches of steel are never identical in chemical composition we need not be surprised that corresponding differences in their behaviour should be observed. By way of illustrating the above mention may here be made of the researches of Diegel,[2] who immersed plates of varying phosphorus content in sea water for twelve months. The plates were metallically connected, and as a result it was invariably found that the metal containing the higher percentage of phosphorus acted cathodically towards that with a lower phosphorus content, and therefore corroded the less. This

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[1] See Chapter XIII.

[2] Diegel, "Verhandlungen des Vereins zur Beförderung des Gewerbfleisses," 1903, 5, 166.

will be evident from a consideration of the following table, in which Diegel's results are condensed:—

No. of Expt.	Conditions of Experiment.	Metal A.		Metal B.		Relative Corrosion $\frac{A}{B}$.
		Phosphorus. Per cent	Loss in Wt. per 100 Sq. cm. (Grm.)	Phosphorus. Per cent	Loss in Wt. per 100 Sq. cm. (Grm.)	
1	Plates A and B in metallic contact in open sea water.	<0·01	10·4	0·09	2·2	4·7
2		<0·01	13·0	0·09	5·2	2·5
3		<0·01	10·2	0·45	1·1	9·3
4		<0·01	15·1	0·45	3·0	5·0
5		0·23	10·7	0·84	1·7	6·3
6		0·23	11·1	0·84	4·4	2·5
7		0·062	12·4	1·08	2·2	5·6
8	Plates A and B in metallic contact in sea water contained in a large trough.	<0·01	4·3	0·09	2·15	2·0
9		0·45	3·7	0·85	2·8	1·3
10		0·23	4·1	0·84	2·2	1·9
11		0·23	3·6	0·84	3·6	1·0
12		0·09	4·0	0·85	2·5	1·6
13		0·062	4·3	1·08	2·7	1·6

The presence of nickel in the iron was likewise found by Diegel to exert a very similar influence, those samples rich in this element always acting cathodically towards those of lower nickel content. The same would appear to be true for hardening carbon.[1] Munroe[2] mentions the case of two cold chisels found in the U.S. Steamship "Triana" in 1874, having been taken from the channel way leading from the jet condenser between the foot valve and the air pump. Both chisels were of steel throughout, the points only having been tempered. During the time of exposure to the sea water in the channel way the chisels had suffered severe corrosion; but the corrosion was confined entirely to the soft untempered portions, the remainder showing no evidence of attack. The corrosion was most pronounced at the line of contact between tempered and untempered metal, showing that galvanic activity had been called into play, the tempered portions of the metal being cathodic to the softer part, and thus remaining immune from attack.

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[1] See Howe, "Trans. Amer. Soc. Testing Materials," 1906, p. 158; Sang, "Proc. Eng. Soc. West Pa." 24, p. 258; Ledebur, "J. Iron Steel Inst." 1878, I, 15; Parker, *ibid.* 1881, I, 39.

[2] Munroe, "J. Iron Steel Inst." 1883, I, 363.

No doubt other elements, besides carbon, phosphorus, and nickel, normally present in steel and in wrought iron exert their own individual influence in this way also, some lowering the potential and others raising it; but very little work has been done along these lines, and further researches are urgently needed.

Referring again to Farquharson's experiments, it will be observed that in the fifth pair the steel corroded from three to four times as much as in the first and third pairs, and the iron practically 20 per cent less. This may be accounted for on the assumption that, at some time during the exposure, a reversal of the polarity took place, so that the steel functioned for a time as the anode and thus underwent corrosion. That such is possible will be evident from a moment's consideration. As we have already remarked, the difference in potential between iron and steel immersed in a liquid is at best very slight. Now the condition of affairs at the moment of immersion of the plates alters very materially as the time proceeds, and this for three reasons:—

1. The liquid medium undergoes a change, for a portion of its dissolved oxygen is removed, and some of the iron passes into solution, thus altering its chemical nature.

2. The anode becomes more or less coated with rust or other oxide and this, as we have already seen in the previous section, is electronegative to iron. Consequently if the layer of oxide is sufficiently impervious, the metal may now function electrically as a solid mass of oxide, in other words it becomes the cathode. The original cathode now becomes the anode and undergoes oxidation in its turn, after which a reversal of polarity may or may not occur again according to circumstances.

3. Commercial irons and steels are rarely perfectly homogeneous. Consequently that metal which is serving as the anode will dissolve more or less irregularly in the liquid

medium, the more soluble portions dissolving out first. After a time the less soluble portions will begin to preponderate and the potential difference between the metal and the liquid will fall. Should it become less than that manifested between the metal, serving as cathode, and the liquid, a reversal of polarity must occur, the original cathode now constituting the anode and undergoing solution in its turn. In time a reversal of polarity may again occur, but this must obviously depend upon local circumstances.

Changes in polarity, such as these, have been carefully studied by T. Andrews[1] who prepared a series of bars of different kinds of steel, measuring 30 inches in length, 3 inches in diameter, and having a total superficial area of 84·8 square inches. These were highly polished and separately connected each with a similar bar of wrought iron, a sensitive galvanometer being included in the circuit. The metals were then immersed in sea water for a period of 300 days and any fluctuations in the relative polarities of the metals were constantly observed and noted. The results obtained are given in the following table :—

Andrews' Experiments Showing the Relative Changes of Polarity when Iron and Steel Bars are Placed in Metallic Contact in Sea Water for 300 Days.

Steels used.	Greatest P. D.[2] of Steels when Electropositive Volts.	Total No. of Days that Steels were positive.	Greatest P. D.[2] of Steels when Electronegative Volts.	Total No. of Days that Steels were Negative.	No. of Interchanges of Polarity.
Cast steel No. 2	0·116	233	0·011	66	1
Hard Bessemer	0·063	104	0·052	101	16
Cast steel No. 1	0·092	246	0·005	53	1
Soft cast steel	0·089	293	0·027	6	2
Soft Siemens steel	0·116	208	0·027	66	4
Hard cast steel	0·045	276	0·033	16	2
Soft Bessemer	0·052	216	0·015	62	4
Hard Siemens steel	0·084	258	0·023	28	2

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[1] Andrews, "Min. Proc. Inst. Civil Engineers," 1884, 77, 323.

[2] P. D. = Potential Difference.

The number of times a reversal of polarity took place with hard Bessemer steel is very striking, and it is important to notice that in the case of every kind of steel used a reversal took place at least once, and more often twice and four times. It will be clear that the relative rates of corrosion of the iron and steel in any pair, as measured by the loss in weight, will vary very considerably according to the length of time during which they undergo observation. For example, suppose the steel were cathodic for the first three days, but anodic for the succeeding four days, the iron to which it was attached being correspondingly anodic and cathodic during the same intervals of time. If the bars were removed and weighed at the end of three days the iron would be found to have corroded far more than the steel. If we had waited until the end of the sixth day, however, it is probable that very little difference would have been observed, for the steel and the iron would each have functioned for half the time as the anode, and for half as cathode. After seven days the balance might easily have been in favour of the iron. This reasoning shows us at once how little reliance may be placed in such cases upon hurried or isolated tests, and will serve to explain many of the conflicting results obtained by thoroughly conscientious investigators.

This frequent change in polarity is easily made visible by means of the ferroxyl reagent, to which reference has already been made.[1] A method of carrying out the experiment will at once suggest itself to the reader.

We are now in a position to understand a large number of curious cases of corrosion which have puzzled engineers and others who have had to deal with large amounts of iron and steel in practical life. It is interesting to note that even 2000 years ago engineers were cognisant of the fact that unsatisfactory results often followed in the wake of attempts to patch up older iron structures with newer material. For example,

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[1] See p. 248.

Pliny,[1] in his "Natural History"[2] writes, "that there is a kind of hallowing iron within the city, called Zeugma, seated upon Euphrates, wherewith King Alexander the Great, sometime bound and strengthened the bridge over the river there; the links whereof, as many as have been repaired and made new since, do gather rust, whereas the rest of the first making be all free therefrom."[3] No doubt engineers would argue then as now that the newer links were made of inferior iron. But from what we have already learned in this chapter such is not necessarily the case, for if the newer links contained a lower percentage of phosphorus and consequently a higher percentage of iron, other things being equal, galvanic action would be set up, the older links being preserved by acting as cathodes to the newer ones, in accordance with the results obtained by Diegel.

Martell[4] mentions that in 1879 he examined a steel-clad ship which was hauled up on the slip-way in the North of England for repairs, after having been in use for less than a year. The steel plates constituting the sheath had been fixed with iron rivets, and were so badly corroded in their neighbourhood that the rivets protruded some distance out beyond the steel. This was particularly observable between the light and load water marks which were alternately dry and wet with sea water. Here the steel had suffered by contact with the iron, which latter metal had evidently functioned as cathode, and thus proved more resistant to corrosion.

Denny,[5] on the other hand, cites a case in which the exact opposite occurred. A steamer was built with an iron frame, the rudder forgings and small plates connected therewith being made likewise of iron, but all the rest of steel. After being in service for a short time it was found that all the iron portions had suffered badly from corrosion, the steel plates remaining almost unattacked.

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[1] Pliny, the naturalist, is generally believed to have been born A.D. 23 at Novum Comum on the southern shore of Lake Larius in N. Italy. He died at the age of 56, in the year A.D. 79.

[2] See Dr. Holland's translation.

[3] Zeugma was a town of Mesopotamia, situate on the western bank of the river Euphrates, where was a well-known passage across the river. It was the Eastern boundary of the Roman Empire, and in Pliny's age a chain of iron was said to extend across it.

[4] B. Martell, "Min. Proc. Inst. Civil Engineers," 1881, **65**, 102.

[5] Denny, "J. Iron Steel Inst." 1881, I, 63.

These, and numerous other instances of a similar nature have frequently been cited as proofs that iron is better than steel, or vice versa, as the case may be. Such arguments, however, are pure rubbish, and the true explanation will be obvious to the reader who has followed the reasoning given above. The remedy for this galvanic corrosion obviously lies in constructing ships, chains, etc., of a uniform kind of metal throughout, or else, if two kinds of metal must be employed, washers of some insulating material should be used to prevent actual contact at the joints.

D. GALVANIC ACTIVITY EXHIBITED BETWEEN IRON AND OTHER METALS.

1. *Iron and Tin.*

In 1835 Sir Humphrey Davy and J. Davy observed that in air tin is electropositive to iron, and that, if the two metals are immersed in sea water, the iron constitutes the cathode, whereas the tin passes into solution as the anode. It was therefore argued that the presence of tin should serve to retard the corrosion of iron. This, however, was soon found to be contrary to experience. Thus in 1836 M. Mulder[1] of Rotterdam placed two iron plates of equal weight in separate glass vessels containing sea water. One plate was free, whereas the other lay in contact with 8·140 grains of tin. After twenty days the plates were cleaned and weighed, the following results being obtained :—

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[1] Mulder, "British Association Reports," 1838, p. 293.

	Plate Free.	Plate in Contact with Tin.
Initial weight of iron plate	32·907 grains	32·907 grains
Final weight of ,, ,,	32·726 ,,	32·674 ,,
Loss in weight	0·181 ,,	0·233 ,,

From this it appears that the plate in contact with the tin lost nearly 30 per cent more in weight than the other.

Van Beck,[1] however, explained this anomaly by showing that, although tin may at first prove electropositive to iron upon immersion in sea water, the polarity soon changes, the iron becoming ultimately positive, thus dissolving away as the anode.

Owing to the ease with which tin may be applied to the surface of iron the process of tinning iron articles has become one of great industrial importance.[2] Now so long as the tin covering remains intact the iron beneath must remain uncorroded. Should, however, the tin covering be incomplete, either through imperfect initial treatment or through subsequent wear and tear, so that the bare iron is exposed, rusting will at once set in, the process being materially hastened by the galvanic currents induced by contact with the tin, in accordance with the observations detailed above.

It is found in practice that the tin surface invariably breaks down at a number of isolated points and not in continuous patches, indicating that it contained a number of pin-holes.[3] When the tin has been freshly put on to the iron surface these pin-holes are generally so small as to elude detection by the naked eye. Their number will of course vary with the mode of application and the thickness of the tin layer, being greatest in the case of the singly treated sheet, and least upon those which have been trebly or quadruply coated. They are not, however, entirely absent even from these, and although a superficial inspection may fail to indicate any lack of continuity in the tin covering, slight pitting invariably takes place. Curiously enough, however, the rust spots usually occur not in the rough and apparently imperfect places, but upon the bright parts where the tin coating appears to be most perfect. The weak places, may, however, be readily detected by the following method, due to W. H. Walker,[1] which hinges on the fact that iron readily dissolves in dilute sulphuric acid, yielding a solution which reacts with potassium ferricyanide to produce an intensely blue coloration (Turnbull's blue). A solution of the following composition is prepared:—

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[1] Van Beck, "Edin. New Phil. J." October, 1837.

[2] An interesting account of the tin-plate manufacture is given by P. Flower, "J. Iron Steel Inst." 1886, I, 36. See also E. Trubshaw, *ibid.* 1883, I, 252.

[3] See Ulzer, "J. Soc. Chem. Ind." 1901, **20**, 127; from Mitteilungen des K.K. Techn. Gewerbe-Museums in Wien, **10**, 203.

"Gelatine	50 grms.
Water	450 ,,
$K_3FeC_6N_6$	1 ,,
H_2SO_4	0·1 ,,

"The gelatine is dissolved in the water by the aid of heat and the ferricyanide added as the reagent is needed; owing to the gradual reduction of the ferricyanide and the action of the acid on the gelatine, the acid should be added only when the gelatine has cooled to about 40° C., and only so much of the reagent prepared as can be used within a few hours. If a large number of plates are to be examined, the sensitiveness of the reaction may be increased by soaking the plates over-night in a dilute ammonium chloride solution, or by dipping them for one half-minute in 5 per cent sulphuric acid. Either of these treatments loosens the material at the bottom of the pin-holes, and allows the iron at these points to dissolve more rapidly." Blue spots therefore appear at such spots upon addition of the prepared gelatine, which renders their detection both easy and certain.

2. *Iron and Zinc.*

Nearly eighty years ago E. Davy[2] pointed out that zinc was capable of protecting iron from corrosion. It can scarcely be maintained that he was the discoverer of this interesting fact, but he certainly was the first to make decisive experiments upon the subject on a large scale, and in consequence his researches deserve due recognition. His work was done under the auspices of the Board of Public Works in connexion with the preservation of iron work—mooring chains, buoys, and such like—in Kingstown harbour. Since then numerous observations have been made bearing out the truth of Davy's results.

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[1] W. H. Walker, "J. Ind. Engineering Chem." 1909, 1, No. 5.

[2] E. Davy, "British Association Reports," 1835.

As we have already seen, zinc is electropositive to iron and when the two metals are placed in contact in a corroding medium, the zinc dissolves away as the anode, whereas the iron, which functions as the cathode, is preserved. Zinc, therefore, serves as an excellent metal for coating iron articles destined to be subsequently exposed to corroding agencies, and the widespread use of so-called galvanized iron bears witness to a universal recognition of this fact. This is the more evident when we remember that in the United States of America alone, no fewer than 60,000 tons of zinc are used annually for galvanizing purposes, the area galvanized amounting to approximately seventy square miles.[1] It will be obvious that imperfections in the zinc coating are not so serious as similar flaws would be in tin plate, for, so long as any zinc remains upon the iron, the latter metal will be perserved. But of course the zinc will not last for ever, and when all has been oxidized the iron must perforce begin to do the same.

W. H. Walker[2] has devised a very useful method by which the presence of pin-holes and cracks in a zinc coating may be detected. "If a piece of zinc," he writes, "be placed in a strong solution of caustic soda heated to about 100° C., no action is noticeable. If now the zinc be touched with a piece of iron, hydrogen is liberated in great volume *from the iron*. That is, iron in contact with zinc in hot, strong caustic soda is a seat for the generation of hydrogen. Hence, if a piece of galvanized iron free from pin-holes and cracks be so treated, no action is visible; if the iron be exposed, however, to even a minute degree, a stream of fine hydrogen bubbles will be seen arising from the surface. Small cracks in the zinc coating may be easily detected in the same way.

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[1] See C. F. Burgess, "Engineering News," 1905, **54**, 352; from "Electrochem. and Met. Ind." 1905, **3**, 17.

[2] Walker, "Proc. Amer. Soc. Testing Materials," 1909, **9**, 430.

"Ordinary hot galvanized ware is generally very free from imperfections of this kind. Wet galvanized material, on the other hand, is frequently very porous, generating hydrogen at numberless small points over its entire surface. Theoretically the best electroplated surface is that carrying the greatest weight of zinc per unit area, deposited at the slowest rate. That is, the lower the current density at the cathode in plating, the less porous will be the deposited metal; and the thicker this dense deposit, the better protection will it be. A great many tests on electroplated zinc coated iron were made, the samples varying in both these particulars. In every case those deposited most rapidly were the most porous, and the results showed that the *time* of plating was more important than the weight of zinc per unit area, although there was a minimum weight below which it was not safe to go."

It has been suggested that lumps of zinc placed in iron boilers should be effective in preventing corrosion. This no doubt is true for those portions of the boilers in actual contact with, and very near to, the zinc, but other portions can obviously not be protected by galvanic activity, for the sphere of influence of the zinc must of necessity be limited. In order to overcome this difficulty zinc paints have been prepared consisting of a liquid vehicle, such as linseed oil, containing a certain percentage of zinc dust as pigment;[1] and it is claimed that iron coated with such paint must be highly resistant to corrosion. Practically, however, the results have been disappointing, nor is the reason far to seek. On oxidation zinc yields a relatively insoluble oxide which is electronegative to iron, thus reversing the electrical polarity of the system; and even though all the zinc pigment in the paint may not have been oxidized, the presence of some zinc oxide is sufficient to set up galvanic action at the expense of the iron leading to rapid corrosion.

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[1] See Mallet, "British Association Reports," 1840, p. 241.

Another way out of the difficulty is to employ complete zinc sheathing. The feasibility of this procedure has been discussed by B. Bell[1] in connexion with the corrosion of ships.

Quite apart from its galvanic activity, zinc has been found useful in retarding the corrosion of boilers in certain districts where the feed water is acid. Richardson[2] refers to the case of certain steel boilers which were supplied with feed water gathered from a district near Oldham where an outcrop of coal measures took place. The result was that unusual corrosion occurred owing to the presence in the water of sulphuric acid, caused by the oxidation of pyrites in the coal. In all these cases, however, the corrosion was arrested by the application of zinc which neutralized the acid. Inasmuch as neutral salts, unless in very concentrated solution, invariably stimulate the corrosion of iron, the mere neutralization of the free acid could scarcely by itself have completely arrested the observed corrosion, and galvanic activity would undoubtedly assist here as in other cases.

3. *Iron and Other Metals.*

Experiments have been carried out with iron in contact with various other metals, such as copper, bronze, nickel, etc., by a few investigators. At present, however, the results obtained are not of great practical importance, and we shall not consider them in detail. For further information the reader is referred to the memoirs listed below.[3]

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[1] Bell, "Trans. Inst. Naval Architects," 1869, **10**, 174.

[2] Richardson, "J. Iron Steel Inst." 1881, I, 67. Parker, J. Iron Steel Inst." 1881, I, 39, alludes to a similar action.

[3] E. Davy, "British Association Reports," 1835, p. 33.
J. B. Hartley, *ibid.* 1837. Notices and abstracts, p. 56.
Mallet, *ibid.* 1838, p. 299; 1840, p. 262.

Thwaite, "J. Iron Steel Inst." 1880, II, 667.

D. Phillips, "Min. Proc. Inst. Civil Engineers," 1886, **85**, 295.

Lindet, "Compt. rend." 1904, **139**, 859.

Dunstan, Jowett, and Goulding, "Trans. Chem. Soc." 1905, **87**, 1548.

Heyn and Bauer, "Ueber den Angriff des Eisens durch Wasser und wässerige Lösungen," Mitteilungen aus dem königlichen Materialprüfungsamt, 1908, **26**, 23.

G. von Knorre "Verhandlung des Vereins zur Beförderung des Gewerbfleisses," 1910, pp. 265, 313.

XV.

THE RELATIVE RATE OF CORROSION OF IRON AND STEEL.

No branch of our subject has been more hotly disputed or made the subject of more numerous investigations by practical men than that which we now pass on to consider. At the same time it must be confessed that a large proportion of the work done has been thoroughly unscientific and unreliable, so that the difficulty of getting at the real truth has been greatly enhanced. The reader, who has studied the preceding chapters with due care, cannot fail to have realized how extremely difficult it is to conduct several series of strictly comparable corrosion experiments with different samples of iron and steel; for the various factors influencing the results are far more numerous and uncertain than is generally realized. Yet this is a task which has been attempted by men with the most laudable intentions, it must be admitted, but also, unfortunately, with a profound ignorance of the most elementary essentials to the conduction of scientific research. Thus, for example, one investigator compares the results obtained by the use of plates of varying sizes, no two being alike. Another connects all his plates together with copper or iron rods, and is surprised to find that some of the plates (those which constitute the anodes) are completely eaten away, whereas others (the cathodes) are scarcely affected. Yet a third cleans some of his plates, but not others, and cannot understand why his results show slight (!) variations. Were it not for the fact that these researches have been undertaken in all seriousness and in evident good faith, a detailed account of the same would no doubt prove very humorous reading to the scientist desirous of indulging in a hearty laugh. Probably no branch of chemical and metallurgical literature bears such unmistakable marks of the hand of the amateur as does this one.

But this is only one side of the question, for a few really admirable researches have been carried out in this field. Before we pass on to treat of these researches, however, let us pause to consider, for a moment, what the whole question really involves

If we were dealing with perfectly pure iron, it would be a matter of indifference in what way the metal was prepared as regards corrosion, for its properties must remain constant provided the metal is eventually brought to the same physical condition.

When, however, we are concerned with such complex mixtures as iron and steel, the matter is by no means so simple, for now we have three factors to consider, namely :—

1. *Chemical Composition.*—We have already learned in a previous chapter that the presence of small quantities of foreign elements in iron exerts an enormous influence upon the corrodibility of the alloy. Now if the influence exerted by each element were thoroughly understood—and there is no reason why, in time, this should not be the case—it ought to be possible, provided the metal is perfectly homogeneous, to state, from a consideration of its chemical analysis alone, in terms of some definite standard, its order of corrodibility. If pure iron were taken as the standard, and its loss by corrosion under certain well-defined conditions taken as 100, that lost by the given sample of metal under precisely similar conditions of exposure might be expressed relatively to this, the number obtained being called the CORROSION FACTOR. Thus, for example, if the pure iron lost 0·10 grm. and the sample to be tested lost 0·12 grm. under *precisely similar conditions*[1] then $\frac{0{\cdot}12}{0{\cdot}10} \times 100 = 120$ is the required corrosion factor under the particular corrosive agencies at work.

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[1] This point cannot be emphasized too strongly.

In comparing, therefore, the relative corrosivity of iron and steel, it is essential that the two metals have an almost identical chemical composition, otherwise there is no point in the comparison. Were chemical composition the only factor to be considered, such a comparison would obviously be unnecessary, for, in such circumstances, two metals of identical composition must corrode at the same rate. We have, however, to reckon with a second factor.

2. *Homogeneity.*—We have already seen[1] that steel is particularly liable to exhibit an irregularity of composition owing to what is known as segregation; consequently galvanic activity is very liable to come into play, rendering the steel highly corrodible. With wrought iron the case is different, for this metal is piled, cross-piled, hammered, rolled, re-rolled, and the like, until it has arrived at a condition of remarkable evenness of composition. Furthermore, as Matheson[2] points out, repeated rolling gives slight films of oxide between the layers. For example, when best Yorkshire iron is torn asunder in the testing machine, forty colour-lines may often be detected for every inch of thickness of the metal, each colour-line indicating a weld. Each of these thin films offers a barrier to corrosion, and on reaching them corrosion has to take a new departure or begin again. Steel rolled out from a cast ingot has, of course, no such lines, and therefore becomes a more ready prey to corrosion.

3. *Physical Condition.*—Strictly speaking we ought not to have this point to consider in this connexion, for the metals to be compared ought to be in the same condition as far as their physical properties are concerned. For instance, neither specimen should be strained, otherwise galvanic activity is sure to render the results uncertain. One metal should not be more porous than the other, and the surfaces exposed to the corroding influences must be as exactly similar to one another as they can be made. Further, compact iron cannot be compared with the powdered metal; and so on. These points will now

[1] See p. 250.

[2] Matheson, "J. Iron Steel Inst." 1909, I, 105.

be obvious to the reader, but they have not always been taken into account by investigators.

From the above it will be clear that the importance of determining the relative rates of corrosion of iron and steel, although very great, has probably been somewhat exaggerated. *If* the steel is properly made it will be thoroughly homogeneous, and its corrosivity will therefore depend upon its chemical composition; and the same, of course, applies to wrought iron. Consequently, a sample of such steel of the same chemical composition as the wrought iron must corrode at the same rate as the iron. The questions which are of supreme importance to us, therefore, are these:—

1. How can we make our steels thoroughly homogeneous? and

2. What is their most suitable chemical composition for the purposes in hand?

The answer to the former question must be left to the manufacturer. In Chapter XIII we have given as complete an answer as possible with our present knowledge, as far as corrosion is concerned, to the latter question. But of course, corrodibility is not the only factor to be considered by the engineer, the strength and elasticity of the materials being oft-times of far greater importance. The influence of foreign elements upon such physical properties as these, however, has been far more thoroughly worked out than is the case for corrosion.

But whilst the author desires to point out that the importance of determining the relative rates of corrosion of iron and steel under different conditions has been somewhat exaggerated, he does not wish to go to the other extreme and deny that it has any real value, for such would be a grave error. It will readily be admitted that our methods of preparing steel and iron are not yet perfect, and it is practically impossible to prepare two batches of metal of more than approximately identical composition and of moderately good homogeneity. The question, therefore, as to which commercial method of preparing iron and steel is giving the best results, is one of very great moment, and deserving of our careful consideration. If the methods are about equally satisfactory, there will be but little difference in the corrodibility of the product—and, as we shall presently see, such is usually the case. This is a matter for congratulation, it is true; but it is not one of finality. We have yet to raise the standard for both the wrought irons and the steels.

ACCELERATION TESTS.

This is an age of rush and hurry. Whereas our forefathers would have been quite content to set up experiments with the object of determining the relative rates of corrosion of different samples of metal, and to wait twenty, thirty, or even fifty years for the result, such a slow method of working is not suited to the temper of the modern scientist. The consequence is that men have cast round in all directions for some quicker method of arriving at the same results, and have devised the so-called *Acceleration Tests.* One of the most common of these is the immersion of the samples to be tested in sulphuric acid, either at the room temperature or at some higher temperature according to the rapidity or otherwise with which the results are required. Sometimes sea water is the corroding liquid medium employed, or solutions of metallic or ammonium salts, of varying concentrations. In this way it is generally believed that reliable results may be obtained, for, it is argued that, by the use of liquid corroding media such as those mentioned above, the natural corrosive influences are imitated and intensified, so that the result must be the same as would be obtained by greatly prolonging the time of exposure. Now this is such an important conclusion to arrive at that we shall do well to consider it carefully before we accept it as correct.

It would appear that such a conclusion is perfectly right so long as we are dealing with an almost perfectly pure metal, free from strain. In such a case, however, comparison is needless, for pure iron is pure iron, and any two samples in the same physical conditions must corrode at the same rate under identical conditions of exposure. But the bulk of the metal used in this country contains numerous impurities. Take, for example, wrought iron—the purest form of commercial iron—which always contains appreciable quantities of cinder, which is itself practically incorrodible. On immersing the metal in a corroding liquid medium we have two opposing factors to consider, namely :—

1. The mechanical protection offered by the superficial particles of cinder which prevent the liquid from coming into contact with the whole of the iron.

2. The extra corrosion induced by galvanic action between the cinder and the unattacked iron.

Now the mechanical protective influence of the cinder will depend upon its area, and this will tend to increase as the surface of the metal is corroded away, as a glance at the accompanying diagram, designed by Howe,[1] will show. In this way one explanation is forthcoming for the fact, noted in Chapter VI that, as the time proceeds, the rate of corrosion decreases.

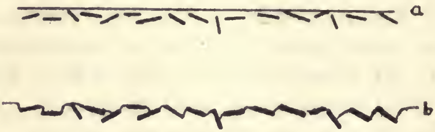

FIGURE 63.—HOWE'S METHOD OF SHOWING THE PROTECTIVE ACTION OF CINDER AS CORROSION PROCEEDS.

On the other hand, we have the galvanic action to reckon with as well, and the actual rate of corrosion must depend upon the resultant of these two factors. Now the galvanic activity is here largely dependent upon the intensity of the potential difference between the iron and its cinder, and, as we have already seen in the previous chapter, this is determined by the nature of the corroding medium. It does not of necessity follow, therefore, that, by intensifying the general corrosive influences by the use of warmth and particularly active media, the two factors mentioned above will be increased in the same relative degree, and that the results are the same as they would be if the metal were exposed for a longer time to less intense action. Consequently the results are not strictly comparable. Of course there are other factors involved, for cinder is not the only impurity in wrought iron, and it is practically absent in good steel;[1] and it is only reasonable to suppose that these will modify the above influences to a considerable extent.

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[1] Howe, "Proc. Amer. Soc. Testing Materials," 1906, **6**, 158.

The thick lines show the plates of cinder, and the thin line indicates the surface of the iron, (*a*) before corrosion, (*b*) after corrosion has proceeded for some time.

We thus see that, from theoretical considerations, acceleration tests may not be reliable. It is interesting to inquire, therefore, what is our experience in practice. It must be confessed that the data are here scanty, but sufficient are to hand to indicate their uncertain nature. Frazer[2] recently determined the relative rates of corrosion of acid and basic steel plates in a variety of ways. When exposed to air, river water, and salt solutions, there was nothing to choose between the two metals.[3] On immersion in dilute sulphuric acid, however, the basic steel had the advantage, the following results being obtained :—

Dimensions of Plates.[4] (Inches.)	Loss by Corrosion of:	
	Acid Steel.	Basic Steel.
3·5 × 3·5 × 1	237	100
3·5 × 3·5 × 0·75	396	100
3·5 × 3·5 × 0·5	108	100
3·5 × 3·5 × 0·25	482	100

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[1] In this latter case, however, cementite probably plays the same part. (Howe, loc. cit.)

[2] Frazer, " J. West Scotland Iron Steel Inst." 1907, 14, 82.

[3] See p. 277. Where the results are given in detail, and discussed.

[4] An analysis of the metal plates used is given on p. 278.

The enormous differences here manifested show that we must regard acceleration tests with due suspicion, and not place too much reliance upon the results obtained by their aid.

From the foregoing it is clear that if we wish to determine what particular grade of metal is most suitable for resisting corrosion under certain well-defined conditions, experiments should be tried under those conditions with the different samples of iron, and the respective merits of the last named judged accordingly.

THE CORROSION FACTOR.

The time has now come when a recognized *Corrosion Factor* might be adopted by the civilized world for the various grades of iron and steel on the market. Nor is the establishment of one such a matter of great difficulty. The most simple method is to compare the relative rates of corrosion of the samples to be tested with that of a pure form of iron under identical conditions, the loss in weight suffered by the last named being taken as 100, and that by the others expressed accordingly.

The difficulty has hitherto lain in procuring a very pure iron, but now that such a metal has been placed upon the market by an energetic American firm, this is no longer an impediment. The metal contains 99·954 per cent of metallic iron and would therefore serve as an excellent standard. In any case, the exact conditions of the test, and the analysis of the standard metal must always be given with the corrosion factor, otherwise little value can be attached to the same.

We shall now pass on to consider the relative rates of corrosion of iron and steel as determined by a number of investigators. Only the more important researches are dealt with in the succeeding pages, however, for reasons explained at the beginning of this chapter, and references are given to the researches of those authors that are worth careful study by the student, but for a consideration of which we have not sufficient space at our command.

THE RELATIVE RATES OF CORROSION OF ACID AND BASIC STEEL.

Practically the only work published on this subject is the excellent memoir by Alexander G. Frazer,[1] who employed pieces of metal measuring 3·5 inches square, and of four thicknesses, namely 1·0, 0·75, 0·5, and 0·25 inch, respectively.

The plates were thoroughly cleaned, to remove all scale, and two holes bored right through the top of each to admit of suspension, after which they were submitted to the following treatments for a period of twelve weeks.

1. *The Atmosphere.*

Two pieces of each kind of steel and of each thickness were placed on top of a building in such a position that their surfaces were fully exposed to the varying weather. The first set was washed and weighed weekly, while the other set was not interfered with until the end of the experiments.

2. *River Water.*

Similar plates of the two steels were suspended in the North Calder in such a manner that they could not come into contact with each other. The spot chosen was relatively deep, so that even in the driest weather the plates remained completely immersed. The river water was very impure, being often polluted with residual dye matter and sewage.

3. *Rock Salt Solution.*

This solution was renewed every four weeks, and had a specific gravity of 1·022. It was made by dissolving rock salt in water.

4. *Common Salt Solution.*

This solution was likewise renewed every four weeks, and had a specific gravity of 1·024.

The metals used yielded the following analyses, and are thus seen to closely approximate to each other in the chemical compositions.

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[1] Frazer, "J. West Scotland Iron Steel Inst." 1907, 14, 82.

COMPOSITION OF THE ACID AND BASIC STEELS USED BY FRAZER.

	Acid Steel.				Basic Steel.			
	1·0″	0·75″	0·5″	0·25″	1·0″	0·75″	0·5″	0·25″
Carbon	0·18	0·185	0·17	0·155	0·225	0·19	0·20	0·145
Silicon	0·016	0·014	0·019	0·017	0·014	0·012	0·014	0·009
Sulphur	0·030	0·032	0·030	0·030	0·030	0·026	0·024	0·028
Phosphorus	0·048	0·054	0·045	0·048	0·038	0·042	0·035	0·026
Manganese	0·49	0·47	0·50	0·50	0·56	0·54	0·58	0·57

The results obtained with these samples are given in the following table, in which the corrosion of each basic steel plate, as determined by its loss in weight, is taken as 100, and that of the corresponding acid steel plate is calculated accordingly.[1] The numbers, therefore, in the columns for the acid steels are the corrosion factors for the steels, using basic steel as the standard, under the particular conditions of the experiments.

RELATIVE RATES OF CORROSION OF ACID AND BASIC STEEL (FRAZER).

Conditions of Experiment.	Corrosion of Basic Steel.	Acid Steel: Plates Cleaned Weekly.				Acid Steel: Plates Undisturbed.				Average Corrosion Factors.
		1″	0·75″	0·5″	0·25″	1″	0·75″	0·5″	0·25″	
Atmosphere	100	110	90	111	82	144	101	104	69	101
River water	100	120	109	93	89	120	91	94	93	101
Rock salt solution	100	111	60	86	48	178	80	95	63	90
Common salt solution	100	109	95	104	87	140	55	148	110	106
Average	**100**									**100**

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[1] It is only fair to state that Frazer does not give his results in this form, but gives the actual losses in weight sustained by each plate—as, of course, an investigator should. The above plan is adopted by the present Author on account of its simplicity to enable the reader to realize at once the relative merits of the two steels. Owing to the numerous mis-

An examination of the above table reveals the following points:—

1. On the average the two steels corrode at precisely similar rates. This, of course, is what we might expect seeing that their chemical compositions are almost identical, provided they are equally homogeneous.

2. On the whole the thicker plates of acid steel had a higher corrosion factor than the thinner ones. The reason for this, however, is by no means clear.

Experiments were also carried out with sulphuric acid as corroding medium, but the results of these have already been considered.[1] The basic steel was found to resist acid attack to a far greater degree than the acid steel, and this result coincides with the experience of J. McMillan.[2]

The Relative Rates of Corrosion of Iron and Steel.

Parker's Experiments.

In 1881 William Parker[3] published an account of a very thorough investigation of the whole question. Eleven different samples of iron and steel were taken and twelve discs, measuring 4·5 inches in diameter and 0·25 inch in thickness, were cut from each. Six discs of each kind were cleaned and polished, the remaining six being turned bright at the edges only, their surfaces still being covered with hammer scale.

The discs were now divided into six series, each series consisting of eleven polished discs, one of each kind of metal, and eleven black discs, likewise one of each kind of metal, that is to say, of twenty-two discs in all. These were attached alternately, one black and one polished, to a long glass rod

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prints in Table VI of Frazer's memoir, in which his results are condensed, the data contained in the table given above are calculated from the figures supplied in Tables I to V of Frazer's memoir.

[1] See p. 275.

[2] McMillan, "J. West of Scotland Iron and Steel Inst." 1907, **14**, 82. In the discussion of Frazer's paper.

[3] Parker, "J. Iron Steel Inst." 1881, I, 39.

strengthened with an iron core. The plates were separated from one another by glass washers, some 0·75 inch long, and were thus protected against galvanic action.

The six series were now subjected to the following treatments:—

Series A was suspended on the roof of a building in London exposed freely to the air and general atmosphere for 455 days.

Series B was securely fixed under water to the pier at Brighton for a period of 437 days.

Series C was secured to the engine-room floors of a ship trading to the East, in such a manner as to be freely exposed to the action of the bilge water. This experiment continued for 240 days.

Series D was suspended in wide water spaces between the tubes of a marine boiler, and situate 12 inches below the water line. The boiler was that of an East Indian Trader, in which zinc was used, and which was blown off as seldom as possible. This experiment continued for 361 days.

Series E was similarly suspended in a steamer engaged in trade with China. Zinc was not used in these boilers. The plates were exposed for 264 days.

Series F was likewise suspended in the boiler of a steam collier plying between Newcastle and London. No zinc was used in the boiler, and water was taken up from a point in the Tyne where the refuse from local chemical works probably acidulated it. The boiler was emptied every ten weeks. The plates were exposed in all for 336 days.

At the conclusion of the experiments, the plates were cleaned and weighed to one $\frac{1}{50.000}$ part of their weight at the Royal Naval College, Greenwich.

We are not here concerned with the corrosion suffered by the black discs, and shall therefore confine our attention solely to the eleven discs of polished metal in each series. The analyses of the metals are given in the accompanying table:—

ANALYSES OF METALS USED BY PARKER.

Kind of Metal.	Mn.	C. (Colour Test.)	S.	P.	Si.	Cu.	Co. N
Parkhead iron	Trace	·09	·027	·316	·020	·060	·15
Skerne iron	·01	·10	·027	·193	·100	·021	—
Leeds forge, best iron	·03	·14	·028	·085	·110	·031	—
Taylor's best iron	Trace	·12	·005	·136	·013	?	·05
Bowling ,, ,,	Trace	·11	Trace	·101	·100	·016	—
Farnley ,, ,,	·01	·11	·012	·096	·090	·016	—
Lowmoor ,, ,,	·01	·10	·022	·142	·120	·022	—
Landore mild steel	·64	·18	·074	·077	·013	·015	—
Brown's ,, ,,	·11	·12	·077	·056	Trace	Trace	—
Bolton ,, ,,	·52	·19	·068	·041	·060	Trace	—
Scotland Steel Co.'s steel	·26	·10	·035	·057	·032	Trace	—

CORROSION FACTORS OF THE VARIOUS IRONS AND STEELS USED BY PARKER TAKING LOWMOOR IRON AS STANDARD.

Kind of Metal.	London Air. A.	Cold Water.		Boilers.			Average Corrosion Factors.
		Sea. B.	Bilge. C.	With Zinc. D.	No Zinc. E.	Collier. F.	
Parkhead iron	94	90	77	67	93	95	86
Skerne iron	91	64	103	72	97	81	85
Leeds Forge, best iron	101	79	88	70	78	102	86
Taylor's best iron	93	93	98	76	91	110	94
Bowling best iron	90	106	96	60	92	100	91
Farnley best iron	100	82	106	79	104	119	98
Lowmoor best iron	**100**	**100**	**100**	**100**	**100**	**100**	**100**
Landore mild steel	124	98	89	138	112	112	112
Brown's mild steel	152	101	104	169	148	127	133
Bolton mild steel	128	93	101	135	120	131	118
Scotland Steel Co.'s mild steel	133	97	94	152	121	124	120

The results of the experiments made with the irons and steels given in the first table on p. 281 are summarized in the second table, in which the loss in weight suffered by the Lowmoor iron in each series is expressed as 100, the losses in weight of the other metals being calculated accordingly.

From these results it is clear that the wrought iron is appreciably more resistant to corrosion than is steel. If we take the mean of all the wrought irons and that of all the steels, the relative corrodibility becomes :—

Wrought iron	100
Steel	133

On examining these factors a little more closely, however, the following points become evident.

1. The various steels and wrought irons resisted the action of cold sea water to the same extent—approximately.

2. The steels suffered decidedly more during exposure to London air than did the wrought irons.

3. The steels differed amongst themselves in their resistivity to corrosion quite as much as they differed as a body from the wrought irons; and the same is true for the last named metals.

On the whole, therefore, the wrought iron would appear to have the advantage, but the difference is small.

Rudeloff's Experiments.

In 1902 Rudeloff[1] carried out a monumental research upon the relative rates of corrosion of two kinds of wrought iron, of Thomas steel, and of Siemens-Martin basic steel. Two sizes of metal were employed, measuring 10 × 50 × 0·075 cm. and 6 × 50 × 0·5 cm. respectively. These were exposed to the following corroding agencies, whilst still covered with mill scale :—

1. *Dry Air.*—This was accomplished by suspending the plates in a specially constructed room, with a rain-proof roof, but with honeycombed brick walls, in such a manner that the fresh air had free access to them all. The air, of course, was only relatively dry.

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[1] Rudeloff, "Mitteilungen aus dem königlichen technischen Versuchsanstalten," Berlin, 1902, **20**, 83.

2. *Weather.*—The plates were suspended in the open, exposed to rain, and the elements generally.

3. *Smoke.*—To this end the plates were suspended in a flue connected with a furnace employed in heating four boilers.

4. *Smelting Furnace Gases.*

5. *Ditch Water.*—The swamp employed for this purpose was 3·2 metres deep, and the test pieces were always under water, although not immersed in mud. The water contained 0·308 grm. of dissolved solid per litre consisting mainly of chalk and magnesium carbonate.

6. *Sea Water.*—The experiments were conducted in the harbour at Munksmarsch.

Five series of both kinds of plates were taken, and weighed at the end of one, three, six, twelve, and twenty-four months respectively. In the following table are given the results obtained with these plates after a two years' exposure to the above influences, the loss by corrosion of the first sample of wrought iron being taken as 100.

CORROSION FACTORS OF IRON AND STEEL RELATIVE TO WROUGHT IRON AFTER TWO YEARS' EXPOSURE (Rudeloff).[1]

Metal used.		Corrosion Factors on Exposure to:					
		Dry Air.	Weather.	Smoke.	Furnace Gases.	Ditch Water.	Sea Water.
Plates 0·5 cm. thick.	Wrought iron	100	100	100	100	100	100
	Wrought iron	200	250	no loss	no loss	150	158
	Thomas steel	200	207	100	600	75	193
	St. Martin steel	200	207	100	300	175	193
Plates 0·075 cm. thick.	Wrought iron	100	100	100	100	100	100
	Wrought iron	146	89	100	67	84	82
	Thomas steel	58	129	200	183	68	96
	St. Martin steel	125	79	100	250	94	113

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[1] Rudeloff expresses his results as percentage losses by corrosion. The numbers in this table are calculated from the data given in Table 49, pp. 176-7 of Rudeloff's memoir.

Here the different samples of steel and wrought iron show quite as much variation among themselves as do the steels as a class and the irons as a class. In other words there is practically nothing to choose between the two metals.[1]

The Experiments of Howe and Stoughton.

In a very valuable communication to our knowledge of this branch of our subject, Howe and Stoughton[2] describe a series of experiments performed with the object of determining the relative rates of corrosion of American iron and steel. The materials consisted of steel skelp (1) of 1897, and (2) of 1906, selected by the authors at the works of the National Tube Company, and (3) of wrought iron skelp ordered from works of high standing. The 1906 steel had been spellerized, and in how far its properties are due to this treatment is uncertain. The results obtained are given in the following table :—

Corrosion Factors of Various Steels Expressed Relatively to Wrought Iron.

Date.	Conditions of Exposure.	Minerals Tested.	Number of Pieces.	Area (Inches.)	Duration of Exposure.	Corrosion Factors.
1897	Sea water	Steel	11	16 × 24	2 years	**117**
		W. I.[3]	12	,,		**100**
1897	River water	Steel	12	,,	2 years	**94**
		W. I.	12	,,		**100**
1897	Weather	Steel	12	,,	2 years	**103**
		W. I.	12	,,		**100**
1897	Weather	Steel	12	,,	8 years	**133**
		W. I.	12	,,		**100**
1906	Hot aerated sea water	Spellerized steel (1906)	12	,,	224 days	**101**
		W. I.	10	,,		**100**

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[1] Other experiments were tried with iron plates attached to ships bound on long voyages, but they are unsuitable for abstraction here. The reader may be advised to consult the original memoir, which is well worth careful study.

[2] Howe and Stoughton, "Proc. Amer. Soc. Testing Materials," 1908, **8**, 247.

[3] W. I. = Wrought Iron.

From these results, which are, undoubtedly, amongst the most complete and reliable that have ever been published, we see that there is really but little to choose between wrought iron and steel. It is remarkable that after exposure to the air and weather generally for a period of eight years the corrosion factor of the steel relatively to the wrought iron should be 133, which is precisely the same number that has been calculated for Parker's experiments in toto.[1] Parker likewise obtained the poorest results with steel which had been exposed to the weather.

One is led to ask, however, whether or not we are justified in assuming that by merely determining the loss in weight we are obtaining a true idea as to its deterioration through corrosion, for this method fails to take into adequate consideration the effect of pitting. For example, a plate in a tank may be perforated by a pit, so that water runs out, even though the plate have lost less than a gram in weight, whereas a second plate, exhibiting greater homogeneity of structure may lose 10 grams in weight and still be serviceable.

So far as the present author is aware, Howe and Stoughton are the only two investigators who have taken this point into serious consideration, and have made practical determinations of the depths of the pits formed. These are given in the accompanying table, and were obtained in the following way:—

The first twelve pieces of steel manufactured in 1906, and ten of wrought iron of similar age, were cut into sheets measuring 8 × 12 inches in area, and immersed side by side in wooden crates in hot, aerated artificial sea-water for a period of 224 days. The plates were insulated to prevent galvanic action. Then the same pieces of steel were re-exposed in like manner for six months along with twelve pieces of steel dating from 1897. As is evident from the table, using the deepest pit in each as a basis of comparison, the 1897 steel pitted on the average considerably less than the wrought iron, in the proportion of seventeen to twenty-eight. The spellerized steel was remarkably free from deep pits.

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[1] See p. 282.

The Pitting of Steel and Wrought Iron (Howe and Stoughton).

Depth of Deepest Pit, Expressed in Inches, for:		
1897 Steel, Immersed Six Months.	Spellerized 1906 Steel Immersed Thirteen Months.	Wrought Iron Immersed Seven Months.
0·008	0·014	0·022
0·022	0·005	0·052
0·062	0·005	0·025
0·007	0·005	0·022
0·018	0·005	0·010
0·005	0·005	0·031
0·021	0·005	0·029
0·016	0·005	0·026
0·010	0·005	0·035
0·102	0·012	—
0·020	0·005	—
0·005	0·009	—
Average **0·017**	**0·007**	**0·028**

CONCLUSION.[1]

It would appear, therefore, that, when everything has been taken into consideration, there is practically nothing to choose between wrought iron and steel as at present manufactured. It is important, however, to learn how far these laboratory experiments are supported by practical experience, before we attempt to dogmatize on the matter.

[1] One or two other researches are worthy of note: Adamson, "J. Iron Steel Inst." 1878, II, 383. D. Phillips, "Min. Proc. Inst. Civil Engineers," 1881, **65**, 73. These last experiments are of little value for purposes of comparison since the surfaces of the iron plates employed were not uniformly cleaned at the beginning. Grüner, "Annals des Mines," 1883, I. Schromm, "Stahl und Eisen," 1892, **12**, 589. Kosmann, *ibid.* 1893, **13**, 149. Otto, *ibid.* 1896, **16**, 561. Diegel, *ibid.* 1904, **24**, 573. J. Collins, "J. Iron Steel Inst." 1879, II, 588. Thwaite, *ibid.* 1880, II, 667. Farquharson, "Trans. Inst. Naval Architects," 1882, **23**, 143. T. Andrews, "Min. Proc. Inst. Civil Engineers," 1885, **82**, 281.

RESULTS OF PRACTICAL EXPERIENCE AS REGARDS THE RELATIVE CORRODIBILITY OF IRON AND STEEL.

1. Howe and Stoughton[1] mention that twenty-nine pipes, all believed to be wrought iron, after long use in the interlocking and signal systems of an important American railroad, were lately examined, with the result that twelve of these pipes were found to be made of steel, the remaining seventeen, only, being iron. The life of the steel pipes was somewhat longer than that of the iron ones. Thus, of those that were practically destroyed by corrosion and pitting :—

Eleven were of steel with an average life of 13·5 years.

Eight were of iron with an average life of 10·4 years.

In this case the steel evidently has the advantage.

2. Howe[2] wrote to the leading British and American shipbuilders, and to American makers and users of locomotive boilers and fire-boxes, asking for their opinion as to the relative resistivity of iron and steel towards corrosion. The replies were as follows :—

Steel more corrodible than iron	7 Firms
No difference	14 ,,
Steel less corrodible than iron	8 ,,
Uncertain	8 ,,

Clearly, therefore, opinions are equally balanced in these cases, and we may assume that there is therefore little to choose between the metals.

3. The Engineer-Surveyors of Lloyd's Register had in 1881 no fewer than 1,100 marine steel boilers running, and it was observed that these behaved towards corrosion quite as well as iron ones. In some of their vessels in which two boilers are working, one of iron and the other of steel, no

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[1] Howe and Stoughton, "Proc. Amer. Soc. Testing Materials," 1908, 8, 259.

[2] Howe, "The Metallurgy of Steel," 2nd Edition, Vol. I, p. 101 (New York, 1891).

difference can be detected, and it is impossible to say which will last the longer.

These, and many other instances might be cited as illustrating the fact that good steel corrodes at much the same rate as good wrought iron.[1]

Important as this conclusion is, we must remember that we have not yet manufactured perfect steel and iron, and that these comparative data will be useless when we pass on in the progress of time to use fresh kinds of steel. As we have already mentioned, it is essential that we first of all determine the influence of the various elements upon the corrodibility of iron, and then try and produce irons and steels of certain compositions which our experiments tell us are best adapted for the particular purposes in hand.

THE CORROSION OF CAST IRON.

Most of the work done upon this branch of our subject has already been considered in the earlier chapters. In many ways cast iron is superior to wrought iron and to steel, especially when it is close grained. Cast-iron piping is well known to have a very long life when properly used, provided the metal is free from blow holes.[2]

Very few researches have been carried out with a view to determining the relative rates of corrosion of cast iron and the other forms of iron. Mention may be made of the results of collecting together all available information by Thwaite[3] in 1880; they are given in the following table:—

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[1] Other cases are mentioned by Snelus, "J. Iron Steel Inst." 1881, I, 66. Ford, "J. Amer. Soc. Naval Engineers," 1904, **16**, 529. Schleicher, "Metallurgie," **6**, 182, 201. T. N. Thompson, "Iron Age," 1908, **81**, 434. Schuhmann, *ibid.* 1908, **81**, 520. Marriott, "Min. Proc. Inst. Civil Engineers," **162**, 213. Cushman, "Iron Age," 1906, **177**, 207. Speller, "Iron Age," 1905, **75**, 741, 1666, 1881. Otto, "Stahl und Eisen," 1903, **23**, 222. G. Johnstone, "Trans., Inst. Eng. and Shipbuilders," Scotland, **45**, 71. Williams, "Iron Age," 1891, **47**, 1109.

[2] See Murdoch, "Engineering News," New York, 1894, **31**, 15. D. Spataro, "L'Industria," **7**, 458, 467.

[3] Thwaite, "J. Iron Steel Inst." 1880, II, 667.

RELATIVE CORROSION OF WROUGHT IRON AND CAST IRON, AS DEDUCED BY THWAITE FROM PUBLISHED DATA.

Metal.	Foul Sea Water.	Clear Sea Water.	Foul River Water.	Pure Air and Clear River Water.	City Air or Sea Air.
Wrought iron	10·450	5·855	7·680	0·655	6·690
Cast iron	3·500	3·386	2·034	0·604	2·637
Cast iron (skin removed by planing)	12·275	4·738	3·884	0·584	4·763

From these results it would appear that the outer skin formed during casting acts as a preservative coating, much in the same way as steel and iron are protected by the film of oxide produced by the Bower-Barff process; for when the metal is planed, corrosion proceeds much more rapidly. This no doubt is the secret of the greater resistance offered by cast-iron pipes to the destructive action of stray electric currents.[1]

FINIS.

We have now reached the end of our study. But the reader who has carefully studied these pages cannot fail to realize that we have as yet only touched the fringe of the subject; in every chapter, nay, on almost every page, fresh subjects for fruitful research may be found; and, should any of his readers be inspired by perusing this work to undertake some investigations for themselves, the Author will feel amply repaid for his labour.

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[1] See H. P. Brown, "Electrical Engineer," New York, 1898, **26**, 441.

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